

VOL. 2 No. 6
DECEMBER 1960

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6 x 9" xx + 675 pages 38 tables 32 illustrations 1960

LIST OF CONTENTS:

1. Development, Present State and Prospects of Organic Spot Test Analysis.
 2. Spot Test Techniques (by Ph. W. West).
 3. Preliminary (Exploratory) Tests.
 4. Detection of Characteristic Functional Groups in Organic Compounds.
 5. Identification of Individual Organic Compounds.
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mass spectrometry

and its use in organic chemistry

by

J. H. BEYNON

Research Physicist, Imperial Chemical Industries, Manchester (England)

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7 x 10" viii + 638 pages 185 illustrations 2 213 refs. 1960

BRIEF CONTENTS

1. Introduction. 2. Instruments. 3. The Measurement of Mass. 4. The Measurement of Ionic Abundance. 5. Ion Production. 6. Sample Introduction. 7. Recording the Mass Spectrum. 8. Qualitative Identification of Organic Compounds. 9. Correlations between Molecular Structure and Mass Spectra. 10. Quantitative Analysis. 11. Other Application of Mass Spectrometry.

Appendix:

1. Table of Masses and Isotopic Abundances for Various Atomic Combinations
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3. Masses and Isotopic Abundances of the Elements

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THE ARC-MELTING OF NIOBIUM, TANTALUM, MOLYBDENUM
AND TUNGSTEN*

A. R. MOSS AND D. T. RICHARDS

*The War Office, Armament Research and Development Establishment, Fort Halstead,
Kent (Great Britain)*

(Received August 9th, 1960)

SUMMARY

An historical survey of the various methods used for arc-melting refractory metals is followed by a discussion on the modern arc-melting processes and techniques, including multiple-melting and semi-continuous casting. Detailed consideration is given to operating conditions in general, deoxidation practices and methods of adding alloying elements. Particular attention is paid to alloy segregation and other defects in ingots and to the means which may be adopted to overcome their occurrence. The authors believe that the most satisfactory method of producing homogeneous high-purity ingots is to combine multiple-melting with the continuous casting technique.

INTRODUCTION

Powder metallurgy techniques¹⁻⁶ and, more recently, slip-casting^{7,8} have been used to produce solid pieces of the refractory materials with satisfactory results, but there is a limit to the size which can be manufactured using these methods. The need for ever-increasing purity has led to the use of arc-melting processes⁹⁻¹¹ which are now complementary^{12,13} to the other fabricating methods. This paper deals mainly with the consumable-electrode arc-melting of ingots up to 3 in. in diameter; the production of large diameter ingots has been discussed by DEUBLE¹⁴ and by TIMMONS AND WINGLING¹⁵.

Little data is available on the arc-melting of W^{16,17}, Ta^{4,18} and Nb^{5,19} but there is a considerable amount available on Mo^{10,15,19-22}. This is understandable since Mo is much cheaper than Ta or Nb, and its strategic supply position and reserves are more favourable²¹. Applications for W as a structural material are restricted by its high density and high transition temperature.

METHODS OF MELTING REFRACTORY METALS

Conventional melting and casting techniques are unsuitable for the production of solid masses of the refractory metals; the chemical reactivity of these metals is such that no suitable refractory is available in which to melt them without contamination.

Processes which may be considered for melting the refractory metals are: floating zone melting^{23,24}; melting with a plasma^{11,25}; electron beam melting^{24,26}; and arc-melting^{9-11,22}. Of these only arc-melting has been used extensively, although there is an indication that greater use may be made of electron beam melting since the

* Presented at the Conference on Niobium, Tantalum, Molybdenum and Tungsten held at the University of Sheffield, September, 1960.

process has been used to produce 3 in. diameter ingots of Nb weighing up to 100 lb.²⁶. Information on the very high temperature plasma-jet is lacking but it is known that melting, cutting and spraying of refractory metals is possible^{11,27}.

HISTORY OF ARC-MELTING

The first consumable-electrode arc-melting furnace has been attributed to HARE²⁸, who, in 1839, used it to melt Pt and conduct various electro-chemical reactions. SIEMENS²⁹ also melted Pt (8 lb. charges) in an arc furnace in 1875. SLAVINOFF³⁰ used a metal-depositing arc, in 1890, to produce steel ingots, but his experiments could not be continued owing to the lack of adequate power supplies. In 1892 MOISSAN³¹ used a carbon-arc-heated crucible to melt a number of refractory metals. Mo alloys were arc-melted by SARGENT³² in 1900. VON BOLTON^{33,34} melted Ta in 1903; his furnace used a water-cooled Ni anode and had provision for vacuum melting. SIMPSON further developed this furnace and between 1903 and 1912 the then huge quantity of 1 ton of fused Ta was produced³⁵. In 1910 the melting of W, Zr and Ti was reported by WEISS³⁶, who used an arc furnace having a cooled metal shell. MOORE³⁷ developed a Bolton-Simpson type arc furnace which could be tilted to permit pouring, and in 1923 he melted U. The M.W. Kellogg Company began to investigate the use of cooled-crucible arc-melting of steels in 1935, but unfortunately their work was not reported³⁸ until 1948. The real interest in arc melting reactive metals stems from KROLL's description³⁹, in 1940, of the arc-melting of Ti. His furnace had a cooled metal shell, a water-cooled W-tipped electrode and a water-cooled copper hearth, with melting carried out under a reduced pressure of hydrogen or argon. PARKE AND HAM²⁰ made important contributions in 1943. Their furnaces were used for the melting of Mo (up to 220 lb.) and W in high vacuum or in argon, etc. These furnaces incorporated several novel features, and many of the present-day furnaces are based on them.

ARC-MELTING PROCESSES

There are two basic types of processes which may be used for the arc-melting of the refractory metals, using (a) a non-consumable or "inert" electrode or (b) a consumable electrode or "consutrode".

Non-consumable electrode process

In the non-consumable electrode arc-melting process^{9,11,40-48} the electrode usually consists of pure or thoriated W, or of C tips attached to water-cooled conductors, and is connected to the negative pole of a d.c. source. The term "non-consumable electrode" is applied to electrodes which, under normal operating conditions, do not melt away during arcing. If, however, a current appreciably higher than the optimum is used, melting (in the case of W) or disintegration (in the case of C) may occur, resulting in severe contamination of the melt. When used at the optimum current there is a slight loss by vapourization. Materials other than W or C may have to be used when pick-up of these elements cannot be tolerated. In some instances it may be necessary to use electrodes of similar composition to the melt, and to use an arc current low enough to prevent rapid melting of the electrode. The term "semi-inert electrode" has been applied to electrodes which, although basically non-consumable, do in fact melt away slowly.

There is a critical range of minimum ambient gas pressure for the non-consumable

electrode arc; this varies from 5 to 40 mm Hg, depending on the materials concerned and on the energy input. Below this range the arc changes over to a glow-type discharge which is useless for melting purposes, but the arc will function at any higher pressure. Because of the restriction of operating pressure range gas removal from the melt may be impaired. The process has a low thermal efficiency and its use is declining⁹, but it can be useful for the preparation of button melts and for skull melting^{11,40,46, q.v.} It has also been used for producing consumable electrodes in the form of first-melt ingots from material which cannot easily be fabricated into electrode form by conventional means. The prime difficulty is not so much making the electrodes but of joining them together to form one of adequate length.

Consumable-electrode process

The consumable-electrode arc-melting process^{9-11,15,20,21} is generally considered satisfactory for small or large diameter ingots. The smallest diameter refractory-metal ingot which can be produced is not known; in the A.R.D.E. the smallest production sizes are 1 in. in diameter⁴⁷. On the other hand Mo ingots 10 in. in diameter and weighing 1000 lb. have been produced¹⁵ and there is no apparent reason why much larger ones should not be produced if the demand arose.

There is much to commend in the consumable-electrode arc-melting process, and the electrode may consist of any metal or alloy capable of being melted and transferred to the pool in a molten state. Because the metal vapour from the electrode tip permeates the entire arc, the process may be used in high vacuum or at any pressure and in any appropriate gas atmosphere²². Deoxidants and alloying ingredients may be added to the pool as an integral part of the electrode or separately in powder form.

Operation in high vacuum is advantageous when the gas content of the ingot has to be kept to a minimum and is essential when deoxidizing with carbon. However, alloys such as Mo-Al cannot be vacuum arc-melted satisfactorily owing to the loss, by evaporation, of the high-vapour-pressure alloying elements. In such cases an inert gas at near atmospheric or somewhat lower pressure has to be used to minimize the preferential loss of alloy. To minimise the gas content of ingots of alloys of this kind they may be double melted. One technique is to produce a well-deoxidized and gas-free ingot of the pure refractory metal in high vacuum and then remelt it together with the alloying element addition in an inert gas atmosphere. Particular care should be taken to use alloy additions of high purity and low gas content.

It is considered that the consumable-electrode process should be used wherever practicable for both production and experimental melts.

Skull melting and casting

In the arc-melting and pouring or "skull-melting" process^{9,11,47-52} a molten bath, produced with the aid of a consumable or non-consumable electrode, is bottom poured or tilted into a mould to form a casting. As the charge is all molten at the time of pouring alloy segregation does not depend on the constancy of alloy feed to the melt, nor on the homogeneity of the electrode. In the past the process has been used mainly for the production of Ti and Zr castings⁴⁷⁻⁵². The process may be used for the refractory metals¹¹ but the thickness of skull appears to increase with the melting point and thermal conductivity of the metal concerned. Because of this a higher efficiency is obtained from the larger-sized skull-melting furnaces.

The applications of skull-melting include the production of shaped castings⁵⁰, the melting of scrap⁵¹ and the preparation of homogeneous master alloys¹¹.

DEOXIDATION

Interstitial impurities, particularly oxygen^{4,12,53-57}, are detrimental to the mechanical properties of the refractory metals because they reduce ductility. Nb and Ta appear to be less affected by these impurities than are Mo and W because of their higher solubility in the former⁵⁸.

Intergranular precipitates of the interstitial impurities are most damaging when present in the form of continuous grain boundary films^{10,12}. The impurities are more innocuous when present in interstitial solution and consideration has been given to increasing their solubility by appropriate alloying⁵⁹, and to the formation of compounds which are randomly distributed as fine particles¹².

Four possible deoxidation techniques have been considered: deoxidation as a result of evaporation of the oxide concerned; deoxidation by hydrogen; deoxidation by a solid where the product of the reaction is a solid; and deoxidation by a solid such as carbon where the product of the reaction is gaseous.

Deoxidation as a result of oxide evaporation

Several researchers^{4,26,53,60-63} have shown that deoxidation of refractory metals occurs as a result of oxide evaporation. This probably explains early observations that multiple remelting of Mo resulted in low oxygen contents. It may also assist in explaining the low (down to 1 p.p.m.) oxygen content of zone-melted Mo²³ when using the electron-bombardment technique.

An important paper by SMITH *et al.*²⁶ has shown that it should be possible to deoxidize the refractory metals by vaporization of their oxides when melting by the electron-bombardment method. They also considered the deoxidizing tendencies in the melting of alloys; for instance the deoxidation of Mo ought to be possible by the vaporization of TiO from Mo-Ti alloys. Experimental work showed that deoxidation of Nb by Zr was possible, the oxygen being removed as ZrO; estimates of the monoxide vapour pressure showed that even at 0.1% Zr, ZrO is 10 times as volatile as NbO. In Nb with C as a deoxidant the loss of oxygen via NbO predominates, so that it was impossible to check the validity of the C deoxidation mechanism. They conclude that the C deoxidation should cease as the C content drops below about 50 p.p.m.

A method for the preparation of high purity Mo without resorting to the addition of deoxidants was suggested⁶⁴ when it was found that portions of ingots produced with an a.c. supply were much sounder than those produced with any other current supply. An a.c. Mo metal-depositing arc in vacuum produces very small globules²², and this results in a greater degree of purification owing to the large surface area/volume ratio. The use of a retractable ingot technique was advocated to ensure that the gases and vapours can be quickly pumped away from the molten pool. The recent studies by ARGENT⁶¹ and TORTI⁶³ add support to the suggestion.

ARGENT⁶¹ has shown that deoxidation of Mo by evaporation of its oxide will be favoured thermodynamically only in the case of very low carbon content melts, but that kinetic factors may make this reaction play a greater part in practice. TORTI's

researches⁶³ have shown that deoxidation of arc-melted Ta is possible by volatilization of Ta_2O_5 . The amount of oxygen removed by this method varies along the length of the ingot when using a fixed mould (non-retracting ingot). At the bottom of ingots 67% of the oxygen could be removed but only 25% at the top. The results could be explained by the condensed film of oxide increasing in thickness as the top of the mould is approached.

Deoxidation by hydrogen

Deoxidation of Mo by a small partial pressure of hydrogen may be possible²⁰ but there is not enough information available on this technique to form a reliable assessment of its value. Apart from the safety aspects one of the main drawbacks of hydrogen deoxidation is that it tends to produce porous ingots; an extreme example of this is shown in Fig. 1. An accurate control of the hydrogen input would be necessary for a balanced reaction.

Deoxidation by a solid where the products of reaction are solid

Deoxidation of refractory metals by a solid such as Al^{10,15,65} which forms reaction products of high melting point is a promising method¹⁰ when arc-melting in an inert gas atmosphere. The method is not satisfactory when melting under high vacuum owing to loss of the deoxidizer by evaporation¹⁰. In addition to Al consideration has also been given to elements such as Be^{*10,15}, Ca^{10,66}, Mg¹⁰, Li^{55,66}, Ti^{55,66}, Zr⁶⁶, Th^{15,58,66}, and the rare earth metals^{15,66,67}.

Microscopical examination of Al-deoxidized Mo shows a random distribution of small rounded particles which are assumed to be alumina¹⁰.

Deoxidation by a solid such as calcium phosphide has been tried but few details are available⁶⁶. In such a method the reaction products would presumably be calcium oxide which would remain in the ingot as discrete particles, and a phosphorus oxide which would evaporate.

Deoxidation with carbon

In vacuum arc-melting deoxidation with C^{10,15,61,68} appears to be the most favoured and satisfactory method at present for Nb¹⁹, Ta⁴, W¹⁷ and Mo^{10,15,61}. The reaction

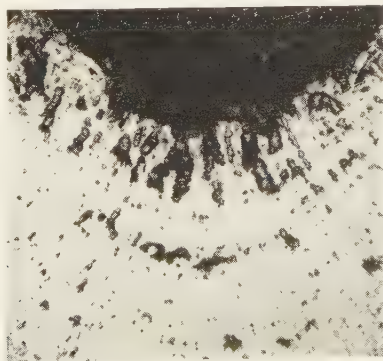


Fig. 1. Gross porosity in a pure Mo ingot melted in hydrogen at 75 mm Hg.

Warning: Be is toxic and elaborate precautions must be taken when using it.

$C + O \rightarrow CO$ and the subsequent removal of gas from the melt are governed by the following factors: (a) temperature of the molten metal; (b) length of time for which metal is molten; (c) turbulence of the molten metal; (d) concentration of free carbon; and (e) partial pressure of CO above the melt. An examination of these factors provides guidance for the optimum operating conditions during melting and also on furnace design, for instance, the partial pressure of carbon monoxide above the melt can be drastically reduced by using a continuous casting technique instead of melting in a long mould.

Deoxidation with carbon is not satisfactory when melting in inert gas atmospheres owing to the excessive porosity produced in the ingots. This is thought¹⁰ to be due to incomplete deoxidation and to the large quantity of carbon monoxide in solution in the melt at the moment of solidification. In contrast to vacuum melting the carbon monoxide is not pumped away quickly, and this results in a high partial pressure above the melt.

The type of carbon used as the deoxidant is important. In the early days of arc-melting Mo defects arose because of the high impurity content and high gas content of the C then used. Electrode carbon of spectrographic purity has been found to be satisfactory¹⁰, especially when it is vacuum-degassed after crushing to the desired particle size and used immediately.

Deoxidation is most efficient when the C is incorporated in the consumable electrode, but this is rarely possible or convenient. Adding C in its elemental form direct to the molten pool is not considered satisfactory since, being of low density, a rather variable quantity is blown away; this results in areas of inadequately deoxidized metal and, in some cases, areas having more than the desired residue of C. Such variations are thought to be responsible for some of the failures during subsequent working. The difficulties may be minimized by adding the C in the form of a high-density master alloy. When produced by arc-melting such an alloy has the advantage of low gas content and high purity.

Because oxygen is more detrimental to the properties of Mo than is C⁵³ it is usual to aim at adding a slight excess of carbon which remains within the ingot as small particles of carbide. There is no doubt that oxygen contents in the range 1 to 5 p.p.m. have an effect on Mo²³; what the lower limit is, if any, is not known²¹. The realm of purity below 1 p.p.m. does not appear to be attainable by arc-melting at present²¹; in any event there is no currently known method of analysing for such small quantities of oxygen.

METHODS OF ALLOYING

The method of adding alloying elements to refractory metal melts to ensure minimum segregation and melting loss presents a difficult problem^{10,11}. There are two basic methods by which the alloy addition may be made when using the consumable-electrode arc-melting process — via the electrode itself or by a separate addition to the molten pool.

Alloy electrodes

It might appear, at first sight, that the most satisfactory method of alloying is to use electrodes which contain all the necessary alloying elements and deoxidants.

Unfortunately this has serious limitations, and in practice can only be carried out with a limited number of alloys¹⁰. Furthermore, unless a large number of ingots of similar composition are required it is not an economic proposition to hold in stock many electrodes of a particular alloy composition¹¹.

Coated electrodes (for example, Mo electrodes electroplated with Ni or Cr) have proved unsatisfactory¹⁰, because the coating may melt before the refractory metal core and drop into the pool in an irregular manner, giving rise to alloy segregation. In the case of Cr, trouble has also been caused by a high-resistance film which impairs the conduction of the current used for arc-melting.

For very small ingots alloying additions, in rod form, may be inserted in refractory metal electrodes which have been drilled along the longitudinal axis. This technique is relatively satisfactory but drilling the long holes is a difficult and time-consuming operation.

Adding alloy direct to the molten pool

Addition of alloys and deoxidants in tablet or pill form direct to the molten pool may be suitable for large diameter ingots, but it cannot be recommended for small ingots owing to the possibility of segregation and the danger of unfused particles remaining in the ingot. The method has been used successfully for the production of first-melt ingots by the non-consumable process and is a convenient means of gauging the amount of material passed into the mould. In this instance the presence of unfused particles in the ingot is not particularly detrimental since they will be completely melted when the first-melt ingot is later used as a consumable electrode to produce a large diameter ingot.

The method of adding alloys and deoxidants in powder form direct to the molten pool is an economic and popular one, but care has to be taken to use the optimum conditions in order to avoid segregation and loss of alloy. It is necessary to ensure that a smooth and continuous stream of powder enters the mould in such a manner that it is evenly distributed over the entire cross section of the mould, otherwise segregation will result. In some alloy melts the upstand (a form of skull) may be as much as $\frac{1}{2}$ in. thick on a 2 in. diameter ingot (Fig. 2) and alloy powder falling on to such a ledge would produce severe segregation.

For several years the A.R.D.E. method¹⁰ consisted of feeding the alloy powder addition to the molten pool by a variable-rate vibrating unit from a hopper inside the melting chamber. This method was abandoned when it was found that the vibration was actually segregating the mixed powders inside the supply hopper, particularly when there were large density differences between the individual powders. The method subsequently employed consists of a conveyor-belt mechanism in which the rate of powder flow may be varied by changing the position of a gauging gate through which the powder passes, or by varying the belt speed. If only a deoxidant or a small amount of alloy has to be added to the melt it is difficult to maintain an even flow rate. This has been overcome¹⁰ by incorporating the deoxidant or alloy powder in a larger quantity of pure refractory metal powder, which serves as a carrier; as the carrier is itself a source of oxygen, due allowance must be made for its deoxidation.

Whatever type of device is used for feeding the powder to the melt, care must be taken to ensure a constant feed rate. Although this fact is generally recognized it is

not always appreciated that variations or drift in the feed rate may arise from changes in the mains electrical supply, or from changes brought about by the ambient temperature of the device.

The particle size of a given powder addition is most important. High-velocity gas streams coming up from the mould blow fine powders away before they enter the molten pool, whilst the use of coarse particles may result in the inclusion of unfused particles in the melt (Fig. 3). Similarly, with a mixed powder addition it is known that, with a certain particle size, there may be an actual division of the high and low density constituents.



Fig. 2. Thick upstand in a Mo-5% Si alloy caused by using too short an arc.



Fig. 3. Segregation of W particles in a Mo-W ingot.

The problem of preferential density segregation can be eliminated by using homogeneous master alloys wherever possible. Failing this the next best technique is to pre-mix the various constituents in fine (micron range) powder size, then produce pressed compacts from this mix. These compacts, which may have to be sintered depending on the cohesion of the powders used, are then crushed and sized. In the absence of a more reliable method of determining the optimum particle size a practical study was made of the behaviour of pure alloy additions of various particle sizes to Mo melts; the consumable-electrode vacuum arc-melting process was used. With the finest powders recovery in the ingot was very small, but increased with particle size. In conjunction with these results cross-sections of the resultant ingots were examined for the presence of unfused or segregated particles. Table I gives the empirically determined particle sizes for several alloying elements.

The addition of ferromagnetic alloys is complicated¹⁰ by the powder adhering to the current-carrying electrode owing to the magnetic field around it. This effect may give rise to pronounced segregation in the ingot.

SEGREGATION

Freezing segregation is inherent during the solidification of any binary or multi-

component alloy because the equilibrium composition of the originating solid phase differs from the composition of the liquid phase. Apart from this metallurgical type chemical segregation there are other factors connected with general arc-melting operations which may also give rise to other forms of segregation.

TABLE I
OPTIMUM PARTICLE SIZE FOR VARIOUS ALLOYING ELEMENTS

Element	Particle size (diam. in mm)
Al	1.8
Ti	1.0
V	0.9
Zr	0.8
Cr	0.8
Co	0.75
Ni	0.75
Nb	0.7
W	0.5
Ta	0.5

Pick-up of impurities

When using preformed consumable-electrodes it is usually necessary to join several lengths together by means of threaded joints. Whenever possible such threads, especially the female one, should be cut dry, or by the carbon dioxide process. If lubricants are used steps should be taken to remove any residue before assembling the rods. Milled slots or holes should be drilled in the female thread to ensure evacuation of the space in the threaded joint.

Powder containers, hoppers and associated piping and joints should be constructed in such a manner that powder cannot remain on ledges, rough surfaces or in corners, and that cleaning, after completion of a melt, is a simple and effective operation. The constructional materials should be of a non-corrodible nature, such as austenitic stainless steel, in order to avoid the pick-up of corrosion products. Pick-up of Fe can originate from the rusty surfaces of mild steel powder mixing drums used for the preparation of deoxidants and alloy addition powder mixtures. Segregation of alloy and of the Fe pick-up can result from insufficient time being allowed for mixing operations. It is known that the optimum mixing time varies according to the type of mixer used and to the mixer volume/mixture volume ratio. Austenitic stainless steel mixing drums are satisfactory and mixing is best done in vacuum, although inert-gas atmospheres have also been used¹⁰.

Infused material in ingots

It is generally assumed that in consumable-electrode arc-melting the electrode is always transferred through the arc to the pool in the form of molten globules. Whilst this is generally true solid pieces can very occasionally become detached from the electrode and fall into the molten pool thereby causing a form of segregation⁶⁹. This is caused by the cathode spot moving away from the tip of the electrode²², fixing on some higher position and melting through the electrode at that point.

When alloying additions are made separately to the molten pool there is always a potential danger of segregation. This may occur in bands (Fig. 4) or in the form of

discrete particles (Figs. 3, 5 and 6); such particles, which may only be partially fused, usually evolve gas which may be trapped (Fig. 5). Fig. 6 shows 3 separate particles of Ti which, although fully fused, have not completely diffused into the Mo.

Base plugs

In order to minimize segregation, particularly in the lower portions of ingots, it is necessary to use base plugs having a chemical composition similar to that of the desired ingot. This may entail making special short ingots or metal-powder compacts



Fig. 4. Band-type segregation in a Mo-Ta ingot.



Fig. 5. W inclusions and associated porosity in a Mo-W ingot; the dark central portion of the inclusion is infused. ($\times 50$)



Fig. 6. Segregation of 3 Ti particles in a columnar crystal in a Mo-Ti ingot. ($\times 10$)

from which suitable base plugs can be machined. Since stock composition base plugs are sometimes used as a starting point the minimum practicable arc-current must be used in order to prevent deep penetration and the associated pick-up caused by dilution.

Depth of molten pool

Moss⁴⁷ has shown that the depth of molten pool in 2 in. diameter Mo ingots can vary from 10 to 45 mm when the current is varied from 1050 to 1800 A using 10 mm diameter consumable electrodes. With a large molten pool, especially in conjunction with magnetic stirring⁴⁷, it is possible to minimise segregation by smoothing out slight irregularities in the flow of added alloy powder; there is also a longer time for fusion, and subsequent diffusion, in the liquid state of added particles, and more time is allowed for deoxidation reactions. Unfortunately no data exists for the liquid/liquid diffusion rates of the refractory metals, but practical experience indicates that this is very small, even at very high temperatures. This is well illustrated in Fig. 7 which shows the effect produced by using an electrode in which a portion was of 50 W-Mo alloy and the remainder pure Mo. It will be noted that there is quite a sharp demarcation corresponding to the change of composition.

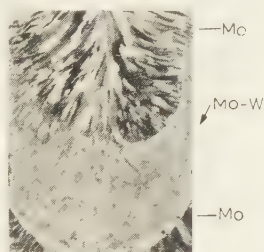


Fig. 7. Sharp demarcation between pure Mo and a 50% Mo-50% W alloy.

Segregation as a result of drift in arc-current supply

A spate of instances of alloy ingots being produced with the alloy content gradually increasing along the length of ingot from the bottom led to an investigation of the causes. The basic reason for the alloy segregation was that the burn-off rate of the consumable-electrode decreased throughout the melting period owing to a drift in output from the motor-generator¹¹, whilst the rate of alloy powder flow was constant. The reduction in current was highest when the ambient atmospheric temperature was low, and vice versa, due to changes in the electrical resistivity of the windings. The technique now used is to run the generators under load conditions for at least 10 min, which is sufficient to produce steady state conditions.

Evaporated films

Yet another form of segregation in alloy ingots, especially when melting in high vacuum, is that due to the evaporation, condensation and subsequent inclusion in the melt of the alloying element addition. This is one of the reasons why inert-gas atmospheres are sometimes preferable for the production of ingots containing alloying elements of high vapour pressure^{10,40} (for example, Al, Mn and Cr).

This type of segregation can be explained as follows. When the tip of a consumable electrode is melted by the high-intensity arc the globules of molten metal are transferred through the arc to the pool. The temperatures of the electrode tip, the globules and the pool are not known, but it is assumed that they may approach the boiling

point of the refractory metal so that rapid evaporation of the alloy can be expected. The vapours move upwards and a portion will condense on the water-cooled mould walls. As melting proceeds the edge of the molten pool comes into contact with the condensed metal vapour on the mould walls and blends with it, giving rise to local edge segregation. At a later stage in the melting process the film of condensed vapour increases in thickness, thus aggravating the segregation, an example of which is shown in Fig. 8. The outer surface of a Mo ingot of internal composition 0.01% C, 0.01% Fe and 0.25% Ti was analysed and showed an average of 1.0% C, 0.15% Fe and 14.0% Ti, with 1.5% C, 5.0% Fe and 34.0% Ti in one region near the top of the ingot. Such segregation has been known to extend $\frac{3}{8}$ in. into a 2 in. diameter Mo alloy ingot.

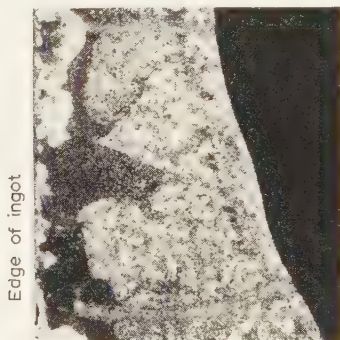


Fig. 8. Edge segregation in the upstand of a Mo-Co alloy ingot.

INGOT DEFECTS

In common with ingots produced by conventional melting processes arc-melted ingots may exhibit defects of various kinds. In view of the high cost of the basic materials, especially Nb and Ta, every possible precaution should be taken to avoid any ingot defect. This obvious truism is given further emphasis when it is pointed out that the raw material alone for a 50 lb. ingot of Nb costs £2500. Fortunately, the principles governing sound ingot production are somewhat similar for all the 4 refractory metals dealt with in this paper; experience on the arc-melting of Mo, the cheapest metal in this group, will give general guidance and such operating data has been published^{10,15,20,22}.

Cracks

Internal cracks are the most serious of the defects found in ingots because they invariably lead to a low yield of sound material after subsequent processing. They are probably caused by an axial tensile stress resulting from the temperature gradient across the ingot during solidification and the consequent differential post-solidification contraction. These cracks may follow the boundaries of the columnar grains, or may cut across the grains; a mixture of the two gives rise to a step-like formation.

Ingot chemistry is an important factor in determining whether or not cracks form and, if they do, the type of cracking. For example, cracks rarely form in properly deoxidized pure Mo but frequently do in undeoxidized or inadequately deoxidized

pure Mo. There is strong evidence to suggest that oxygen, in oxide form, causes a decrease in cohesion between grains, and that internal shrinkage stresses are sufficient to cause rupture; the precise mechanism by which this lack of cohesion is initiated has not finally been established, nor has the temperature at which the cracks are formed. Insufficient data are available to indicate the cracking propensities of alloy ingots, but pure Mo and W are more prone to cracking than Nb and Ta.

Practical experience indicates that ingot cracking may be minimized by ensuring adequate and even deoxidation, by avoiding chemical segregation, and by keeping the cooling rate as low as practicable. The effects produced by varying the cooling rate of Mo ingots have been studied by HOPKIN *et al.*¹⁰, and later work by the present authors, over a much wider range of cooling rates, has confirmed their findings. In the latter work the slowest cooling rate was obtained by lining the water-cooled Cu mould with a 0.1 in. thick press-fitted graphite sleeve. A Mo ingot produced in such a set-up was analysed, and apart from a thin, but not detrimental, film of carbide on the outer surface there was no carbon pick-up. Attempts to reduce the cooling rate further by having a gap between the Cu mould and the graphite sleeve resulted in complete solution of the graphite in the Mo; a similar result was obtained by using a thick press-fitted sleeve. The technique of using a thin press-fitted graphite sleeve has been used to reduce the cracking of Cr-rich alloy ingots.

Porosity

Ingot melted without a deoxidizing addition are generally porous. The addition of a deoxidant such as C, however, results in a much sounder ingot¹⁰. HOPKIN *et al.*¹⁰ have shown that the main cause of porosity in undeoxidized Mo ingots is oxygen

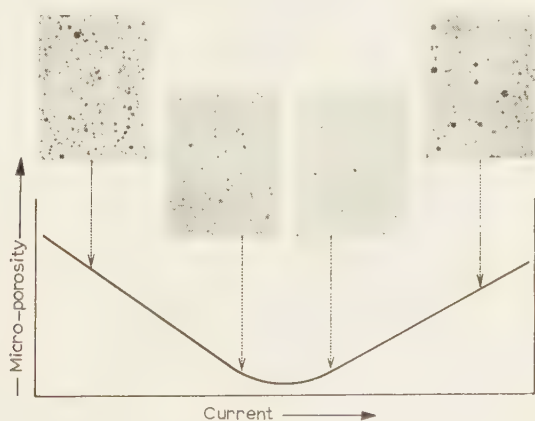


Fig. 9. The relationship between arc-current and micro-porosity in undeoxidized Mo ingots.

in solution. It is probable that most of the oxygen in the melt is in the form of MoO_2 , which gives rise by slow decomposition to free oxygen, the greater part of which comes out of solution on the solidification of the metal.

Studies, as yet uncompleted, are being made of the effect of burn-off rate (which is related to the arc-current) on the degree of porosity in 2 in. diameter ingots made

without deoxidizing additions, using $\frac{3}{8}$ in. diameter pure Mo electrodes on d.c. negative polarity in high vacuum. The tentative results show that the micro-porosity first decreases with increasing current to a minimum, at about 1600 A, and then increases with current increase (Fig. 9). Similar experiments indicate that less porosity is produced with an a.c. supply whilst more porosity results when the electrode is connected to the positive pole of a d.c. supply. These results could be partially explained by considering the size²² of the molten globules produced by the different current supplies.

In C-deoxidized melts produced in vacuum some CO remains in solution in the molten metal until the time of freezing, as a small partial pressure of CO always exists above the melt. This equilibrium solubility of CO is thought to be responsible for the micro-porosity found in all C-deoxidized ingots. Attempts to deoxidize Mo with C in an inert gas atmosphere result in excessive porosity owing to the higher partial pressure above the melt.

Unless precautions are taken to minimize the gas content of powder additions and adsorbed gas films on electrodes, porosity can be expected.

Defects resulting from momentary arc extinction

Arc instability or momentary extinction of the arc may produce a defect in which



Fig. 10. Rolling cracks corresponding to a change of grain structure.

the continuity of columnar grain growth in an ingot is interrupted. This occurs when a metal-depositing arc restrikes on to a molten pool which has started to solidify. Fig. 10 shows a cross-section of a C-deoxidized Mo ingot which cracked during rolling. It will be noticed that cracking commenced at points coinciding with areas of equiaxed structure. The precise cause of failure is not known, but it could be postulated that cracking resulted from stress concentrations caused by differential shrinkage, or from localised areas of high impurity content. Examination of the autographic electrical

records, made during the melt, showed that the arc had been extinguished, for some unknown reason, on two occasions, the arc extinction corresponding to the change in macro-structure. Had the arc been extinguished for a longer period of time it could be assumed that cold shuts would have resulted.

OPERATING CONDITIONS

Electrode size

The selection of the size of a consumable electrode is a controversial matter as there are several valid arguments in favour of using either a large or a small one. In practice the choice is sometimes governed by the availability of ancillary equipment and the methods used to produce the electrode, which may be of circular or square cross section. Small size electrodes facilitate rapid pumping away of gas from moulds; with larger electrodes the conductance path is reduced and this raises the partial pressure above the molten pool. This, however, is not significant unless the electrode diameter is more than one-third the diameter of the mould.

The minimum size of electrode is determined by the current it has to carry in order to produce a satisfactory ingot. If an electrode of a given material and density is too small in diameter excessive temperature will result from ohmic heating; the distance between the current pick-up contacts and the base plug should be as short as possible. A small diameter electrode usually produces a more stable arc than does a large electrode because a relatively centralized heat source is produced even when the cathode spot wanders over the tip. The maximum electrode size is governed by the internal diameter of the mould and by the desired clearance between the electrode and the mould wall.

Examples of the size range of consumable electrodes used to produce several sizes of refractory metal ingots are given in Table II, and some detailed melting conditions are given in Table III.

TABLE II
SIZES OF ELECTRODES USED TO PRODUCE REFRACTORY METAL INGOTS

<i>Ingot diam. (in.)</i>	<i>Electrode diam. (in.)</i>
1	$\frac{3}{8}$
2	$\frac{3}{8}$ to $\frac{3}{4}$
$2\frac{1}{2}$	$\frac{1}{2}$ to $1\frac{1}{4}$
3	$\frac{1}{2}$ to $1\frac{3}{4}$

When double-melted ingots are to be produced it is sometimes convenient to remelt the first-melt ingot in the as-cast state; in this event a small initial electrode diameter is essential in order that the first-melt ingot may also be of small diameter. For example, $\frac{3}{8}$ in. diameter Mo electrodes have been used to produce 1 in. diameter ingots; these may then be remelted to produce ingots between $2\frac{1}{2}$ and 6 in. diameter.

Electrode polarity and burn-off rates

In consumable-electrode arc-furnaces both a.c. and d.c. supplies have been used for melting the refractory metals, but there is no general agreement as to which is the better supply for a given set of conditions. In view of the practical importance

of electrode polarity and burn-off rates the paucity of detailed literature on the subject is surprising.

With a d.c. supply electrode polarity is determined by the nature and pressure of the gas atmosphere used and by the metal to be melted. With alternating current the total arc energy is not necessarily shared equally by the consumable-electrode and the molten pool owing to possible rectification effects.

The use of d.c. electrode-negative polarity produces the most stable arc in vacuum and argon atmospheres and, when the burn-off rate is adequate, gives rise to satisfactory melting conditions^{10,22}. In contrast, a d.c. electrode-positive arc is not as

TABLE III
A. MELTING CONDITIONS FOR PURE REFRACTORY METAL INGOTS

<i>Metal</i>	<i>Atmosphere</i>	<i>Ingot diam. (in.)</i>	<i>Electrode diam. (in.)</i>	<i>Polarity</i>	<i>Current (A)</i>
Mo	Vacuum	1	3/8	Negative	1000-1300
Mo	Vacuum	1 3/4-2	1/2	Negative	1300-1700
Mo	Vacuum	3	1	Negative	1500-2000
Mo	Argon	2	1/2	Positive	2000-2300
Ta	Vacuum	2	1/2	Negative	1400-1700
Nb	Vacuum	2	1/2	Negative	1200-1600
W	Vacuum	2	1/2	a.c.	2200-2600

B. ALTERNATIVE MELTING CONDITIONS FOR PURE REFRACTORY INGOTS

<i>Metal</i>	<i>Atmosphere</i>	<i>Ingot diam. (in.)</i>	<i>Electrode diam. (in.)</i>	<i>Polarity</i>	<i>Current (A)</i>
Mo	Vacuum	2	3/8	a.c.	1900-2300
Mo	Vacuum	3	1/2	a.c.	2200-2800
Mo	Vacuum	3	1	a.c.	3000-4500
Mo	Argon	2	1/2	a.c.	2100-2400
Ta	Vacuum	2	1/2	a.c.	1800-2300
Nb	Vacuum	2	1/2	a.c.	1800-2200
W	Vacuum	3	1 1/2	a.c.	2900-3500

stable^{10,22}, and the cathode spot may wander on to the mould wall, especially when melting in vacuum. If this occurs melting must be stopped at once to prevent mould damage. Although this difficulty has been experienced in the A.R.D.E. with moulds of up to 3 in. diameter SMITH⁷⁰ had no trouble when using a 4 in. diameter mould. The foregoing suggests that the wandering tendency of the cathode spot may be related to the mould diameter; this is theoretically feasible. In the A.R.D.E. cathode spot wander has never been experienced when using d.c. electrode-positive polarity in an argon atmosphere, possibly because the voltage gradient of an argon arc is higher than that of a vacuum arc^{10,22,69}. From a melting point of view a.c. arcs are stable and no serious instance of arc wander has been encountered in argon atmospheres or in vacuum. When using an a.c. supply the distance between the molten pool and the current pick-up contacts should be kept as short as possible, the reason being that this supply often induces an oscillatory motion in the electrode. This motion may give rise to 3 detrimental effects: (a) in small diameter moulds the electrode may touch the mould walls; (b) a thick spatter shield may be produced; and (c) the electrode may break (usually at the joints) particularly when using Mo or W.

In addition to arc stability the burn-off rate is also of importance in controlling

not quality. It is not possible to correlate the burn-off rates for the different metals reported in the literature owing to the differences in the experimental conditions used. Even with standardized conditions significant variations in arc characteristics²² and burn-off rates may be found between different electrodes of the same metal. The values given in Fig. 11 have been obtained in the A.R.D.E. under carefully standardized conditions using autographic recorders for the electrical values. The $\frac{3}{8}$ in. diameter high-purity high-density electrodes used were produced by forging and swaging pressed and sintered metal-powder compacts; they were melted at a pressure of 10^{-3} – 10^{-4} torr.

arc length

In order to maintain satisfactory melting conditions it is necessary to control the arc length within fairly close limits; this may be done manually or by means of some automatic device. For the production of pure refractory metal ingots up to about 1 in. diameter, using $\frac{3}{8}$ or $\frac{1}{2}$ in. diameter consumable-electrodes, the optimum arc length is between $\frac{1}{2}$ and $\frac{3}{4}$ in. It is frequently necessary to use a longer arc for some alloy ingots in order to prevent the formation of upstands of the type shown in Fig. 2. Upstands are caused by high velocity gas streams from the arc blasting very fluid metal up the sides of the mould where it solidifies. With Mo–C alloys, which appear

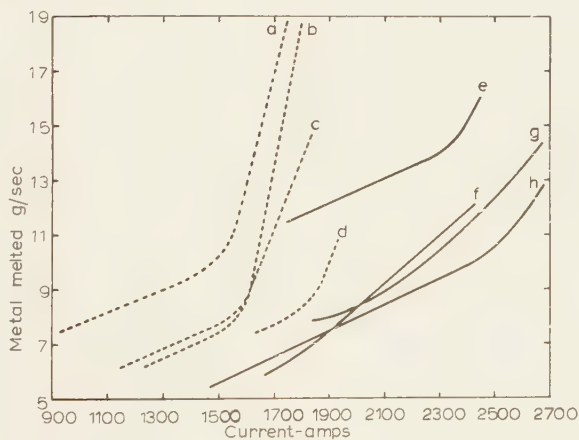


Fig. 11. Burn-off rates for $\frac{3}{8}$ in. diameter refractory metal electrodes in vacuum: (a) Nb, d.c. negative; (b) Ta, d.c. negative; (c) Mo, d.c. negative; (d) W, d.c. negative; (e) Ta, a.c.; (f) Nb, a.c.; (g) W a.c.; (h) Mo, a.c.

be extremely fluid in the molten state, the optimum arc length has been found to increase with the C content.

The use of too short an arc reduces the free-flow diameter of the molten pool and increases the likelihood of "stick-ins", *i.e.* a short circuit between the electrode and the molten pool. Too-short arcs increase the possibility of thick upstands being formed, and these may result in a heterogeneous crystal structure, alloy segregation and, in extreme cases, may lead to side arcing; in this event melting must be stopped to avoid damage to the mould. The use of arcs appreciably longer than the optimum results in excessive spatter and in inferior ingots with poor surface quality, and greatly increases the possibility of side arcing particularly when low current densities are used. Another

disadvantage of using an unnecessarily long arc is that a lower thermal efficiency results; the loss is smaller in vacuum than in a gas atmosphere such as argon. Several workers have stated that the optimum arc length should be smaller than the gap between the electrode and the mould walls. Whilst this is a desirable precaution it is not always practicable.

It is important that the correct arc length should be used in conjunction with a current value within the optimum range.

The flow of molten refractory metals in moulds

When producing ingots with the consumable-electrode arc-melting process it is necessary to ensure an even flow of molten metal right up to the mould walls, in order to minimize scalping losses. The relationship between the diameter of symmetrical metal flow in a mould and the current value used is influenced by the energy distribution between the poles and by heat losses⁶⁹.

The curves⁶⁹ shown in Fig. 12 represent average free-flow diameters obtained in water-cooled Cu moulds with $\frac{3}{8}$ in. diameter electrodes of pure Mo and using a nominal arc length of $\frac{5}{8}$ in. The superimposed solid lines in the curves (Fig. 12) show the desirable current ranges for routine production of high quality ingots of $1\frac{3}{4}$ -2 in. diameter. It will be seen that current values much higher than those required for a specific free-flow diameter are advised. This is because the heat content of the molten pool must be high enough to ensure complete freedom from cold shuts adjacent to the mould, and also to permit impurities to rise to the top of the molten surface. With a d.c. supply in vacuum best results are obtained when the electrode is connected to the negative pole except in the case of W for which an a.c. supply is advisable. As sound ingots are not always produced when using d.c. electrode positive in vacuum, and as mould life is short, this polarity cannot be recommended. The use of an a.c. supply in vacuum produces ingots with the least micro-porosity but high current values are necessary to achieve this.

In argon at atmospheric pressure consumable electrodes of pure Mo have to be used on positive polarity because of the very low burn-off rate when used on negative polarity.

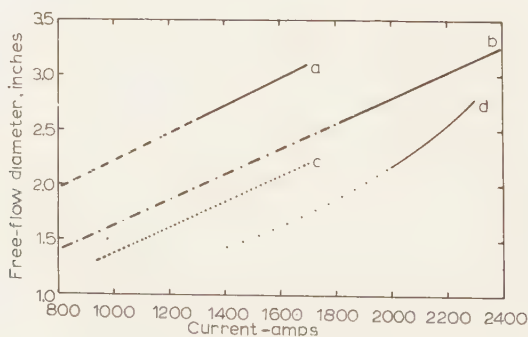


Fig. 12. The relationship between free-flow diameter and current using $\frac{3}{8}$ in. diameter Mo electrodes: (a) d.c. arc, consumable-electrode negative in vacuum; (b) a.c. arc, in vacuum; (c) d.c. arc, consumable electrode positive in vacuum; (d) d.c. arc, consumable-electrode positive in argon. The solid lines indicate recommended current ranges for the production of $1\frac{3}{4}$ -2 in. diameter ingots.

Experience has shown that when using pure refractory metal electrodes of $\frac{3}{8}$ to 1 in. diameter the maximum diameter of satisfactory ingots is, in general, 5 to 6 times the diameter of the electrode used.

THE AS-CAST MACRO-STRUCTURE OF INGOTS

Examination of pure refractory metal ingots has shown that except for a small zone of equiaxed crystals which may be present at the top of the ingot, the macro-structure is wholly columnar⁴⁷. As the vertical mould walls are chilled and the hottest portion of the molten pool is at the centre top, the temperature gradients normal to the growing surfaces are always greater than those parallel to the growing surface; thus, according to NORTHCOTT⁷¹, conditions favourable to columnar growth exist in the melt. The fact that columnar growth is in a direction normal to the solidus contour is of particular practical significance because the shape of the molten pool and hence the liquid-solid interface can be varied considerably by changes in the heat input, *i.e.* mainly the burn-off rate. The factors affecting the grain structure of as-cast Mo have been considered in detail by Moss⁴⁷, who showed that the columnar grains are parallel in shape. His paper also shows how the fineness of the as-cast structure of Mo ingots is affected by the amount and the nature of added alloying elements, and by the cooling rate.

SEMI-CONTINUOUS CASTING

In the semi-continuous or retractable-ingot technique the ingot is withdrawn from the bottom of the mould as it is produced. The molten pool is nominally in a fixed position, usually close to the top of the mould. In contrast is the more common method of arc-melting, where arcing commences at the bottom of the mould, in which the position of the molten pool rises as the ingot builds up in the mould. From a comparison of the 2 methods it will be appreciated that semi-continuous casting offers several advantages. Because the molten pool is almost directly exposed to the main chamber gases and vapours can be quickly pumped away. This results in efficient deoxidation and a reduction of the gaseous and volatile impurity content of the ingot. The small mould area above the melt reduces the tendency for condensed films of evaporated material to form so the possibility of alloy segregation in the outer portion of the ingot is minimized. In addition to enhancing ingot quality the use of semi-continuous casting techniques is often more economical.

Experience with arc-melting processes in general has shown that visual observation of the molten pool is desirable, especially when alloy ingots are being made. In semi-continuous casting the arc and molten pool can be seen clearly at all stages of melting regardless of the length of ingot.

In the A.R.D.E. semi-continuous casting unit ingots up to 36 in. in length and between 1 and 2 in. diameter may be produced using $\frac{3}{8}$ in. diameter consumable electrodes. The 1 in. diameter ingots may be used as electrodes to produce second melt ingots of up to 4 in. diameter.

MULTIPLE MELTING

When it is necessary to ensure a greater degree of purity and homogeneity than could be obtained by a single melting operation the technique of multiple-melting is em-

ployed^{9,11,12,21,53,60}. In production practice double-melting is usually adequate. The beneficial effects of remelting have been known for many years, probably from the early days of button melting. It was then common, and very necessary, to turn the specimen over, and remelt it, several times. An outstanding example of double-melting in vacuum is found in the production of Ti and its alloys⁹; this became especially necessary when, in 1953, it was found that hydrogen was detrimental to the mechanical properties.

The usual routine for remelting is to use either the consumable or non-consumable electrode arc-melting process to produce a first-melt ingot, and then to use this as a consumable electrode for the second melting operation. Similarly, the second-melt ingot, in the as-cast or wrought form, may be used to produce triple-melted material. Each melting operation is usually done in a separate furnace, but equipment has been designed to permit double-melting in one operation⁹. There is a certain loss of low-vapour-pressure constituents at each melt, and experience will show the amount of allowance which should be made for this loss at the commencement of the melt. It has been observed that arc stability decreases with increasing purity of the electrode when consumable electrodes of pure refractory metals are used. This can be overcome by using a higher value of arc current.

The authors believe that the most satisfactory method of producing homogeneous high-purity ingots of the refractory metals and their alloys is to combine multiple-melting techniques with the continuous casting technique. KIEFFER AND PIPITZ¹² support this (for Mo) by stating "It has been established that, without exception, a considerable improvement in both rolling and forging properties results from employing the multi-melting method."

ACKNOWLEDGEMENTS

Acknowledgements are made to Dr. L. NORTHCOTT and Mr. S. W. HOLLINGUM under whose direction the work was carried out and to the assistance of Messrs. B. L. V. JEFFERY and D. L. POWELL.

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RECENT PROGRESS IN PROTECTIVE COATINGS FOR MOLYBDENUM*

P. J. CHAO, D. K. PRIEST AND J. R. MYERS

*Pfaunder Permutit Inc., Rochester, N. Y., and Wright Air Development Division, U.S. Air Force,
Wright-Patterson A.F.B., Ohio (U.S.A.)*

(Received August 24th, 1960)

SUMMARY

Molybdenum base alloys appear promising for aerospace applications where temperatures encountered are between 2000 and 3000°F. Paramount of the challenges limiting the extensive use of molybdenum base alloys is that of preventing catastrophic air oxidation at elevated temperatures.

Protective coatings have been developed for molybdenum base alloys, with the most advantageous coating technique being that of pack cementation. Existing pack cementation techniques do not produce the required coating integrity, and the present research effort was undertaken to obtain a more reliable and reproducible coating system.

An extensive screening study of various pack cementation coating systems was made using three general process concepts. Six promising systems were evaluated in detail. A discussion of the six coating systems is presented together with test results under both room and high temperature conditions.

BACKGROUND

Man's enormous step from comparatively low altitude flight into the higher reaches of the atmosphere and beyond has created the need for materials to satisfy unprecedented requirements. Although significant performance improvements have been made in the super-alloys of iron, cobalt and nickel base during recent years, these alloys are still limited to applications at very low stresses where operating temperatures approach a maximum of 2100°F. Stresses that would be encountered in many structural applications reduce this allowable operating temperature to approximately 1850°F. Temperatures associated with future Air Force vehicles, especially those re-entering from orbital or planetary missions, far exceed those values, and thus the design engineer can no longer select "off-the-shelf" materials for their construction.

Attention is therefore directed to the metals with melting temperatures in excess of 4000°F. Although a large number of metals exist that meet this prerequisite, geological availability reduces this group to four worthy of further consideration. These are the refractory metals niobium (m. p. = 4380°F), molybdenum (m. p. = 4730°F), tantalum (m. p. = 5425°F), and tungsten (m. p. = 6170°F).

* Presented at the Conference on Niobium, Tantalum, Molybdenum and Tungsten held at the University of Sheffield, September, 1960.

A significant amount of alloy development has been completed on the refractory metals of niobium and molybdenum base, and it appears at this time that these alloys can satisfy most of the materials requirements for the temperature range 1850–3000°F. The most important of these alloys are listed in Table I. It will be seen from the data presented in Fig. 1 that this temperature range can be most advantageously satisfied

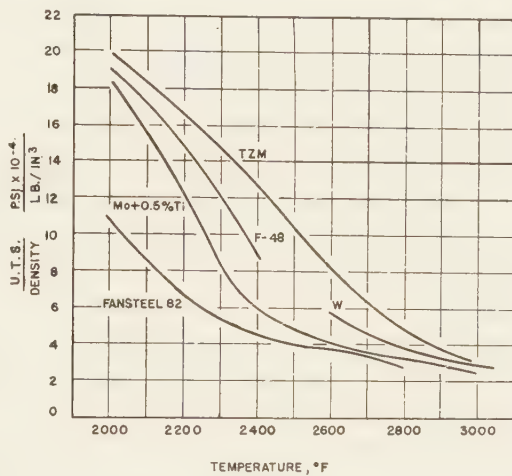


Fig. 1. Ultimate tensile strength to wt. ratio for selected refractory metals (uncoated sheet material).

TABLE I
SELECTED Nb AND Mo BASE ALLOYS

Alloy	Composition
TZM	Mo + 0.5% Ti + 0.07% Zr
Mo-0.5 Ti	Mo + 0.5% Ti
F-48	Nb + 15% W + 5% Mo + 1% Zr
F-50	Nb + 15% W + 5% Mo + 1% Zr + 5% Ti
F.S.-82	Nb + 33% Ta + 0.75% Zr

of molybdenum base alloys. This does not infer that niobium base alloys cannot satisfy many requirements at temperatures approaching 2500°F; nor is it expected that molybdenum base alloys can be extended to applications above 3000°F, where tungsten, graphite, and ceramics become advantageous.

Having selected molybdenum base alloys for applications in the 1850 to 3000°F range, it becomes necessary to consider other properties before they can be fabricated into components for advanced Air Force vehicles. A relatively high ductile-to-brittle transition temperature, susceptibility to air oxidation at elevated temperatures, poor welding characteristics, and unreliable sheet material quality and delivery of molybdenum base alloys limit their use at this time. Because it is believed that the major limitation to the application of molybdenum base alloys is the oxidation problem, only this subject will be discussed.

At temperatures over about 1300°F, molybdenum and all high strength molyb-

denum base alloys suffer air oxidation in excess of that which can be tolerated (Fig. 2), and it is necessary that they be protected with coatings. In comparison, niobium base alloys, tantalum, and tungsten oxidize at a less rapid rate, but they also must be protected by a reliable impermeable coating.

Various coating techniques have been developed for protecting molybdenum base

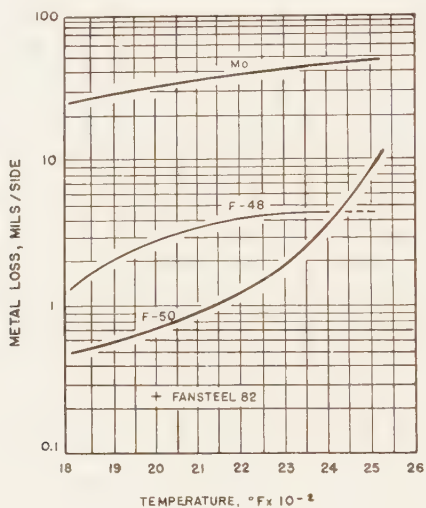


Fig. 2. 1-h oxidation of Nb and Mo base alloys.

alloys from catastrophic air oxidation. The most important of these are: (1) hot dipping; (2) hand troweling; (3) solution ceramics; (4) spraying, including cathode sputtering, gas plating, vacuum deposition, hydrocarbon-oxygen flame spraying, and arc plasma jet flame spraying; (5) cladding; and (6) pack cementation, including chromizing, titanizing, siliciding, and combinations thereof. Each of these techniques presents various advantages and disadvantages depending upon the component to be coated and the end-use application. However, the most promising coating technique for protecting molybdenum base alloys is one in which the coating is formed in place, *i.e.*, one in which the coating is metallurgically bonded to the substrate during the coating process and becomes an integral part of the base material. This can be most successfully accomplished by the pack cementation (vapor decomposition) process.

Several pack cementation coatings have been developed in recent years for protecting molybdenum base alloys from air oxidation at elevated temperatures. However, these coatings were developed through more or less "trial and error" techniques and left much to be desired with respect to coating optimization, reliability, and reproducibility. The latter statement is supported by the data of a large number of government and industrial organizations in the United States which have evaluated these coatings and observed large discrepancies in their comparative test results. It was thus decided to initiate the research effort to be described in this paper in

der to: (1) obtain a complete understanding of the coating process variables; (2) develop an optimized pack cementation coating system; and (3) make available the reliable, reproducible, and optimized coating required for future Air Force applications.

THE CEMENTATION PROCESS

In general, the coating systems investigated may be classified as silicide coatings. These protective metallic coatings are basically diffusion coatings. The coating process involves reduction, deposition, ion interchange, diffusion, and the formation of new compounds. The coatings, then, are solid solutions, or inter-metallic compounds, or both, and are composed of alloys of the coating materials and the substrate. They are an integral part of the base metal and so bonding strength is excellent. The properties of these kinds of coatings can be controlled by a careful choice of the elements in the system and by proper control of the thermodynamics and kinetics of the reaction.

In this work cementation coating procedures employed only the pack process because of the practical end-use difficulties of the vapor streaming process. The pack process is carried out by packing the objects to be coated in a mixture consisting of: the coating metals in elementary form or in a combined form which can readily react at elevated temperatures; a carrier compound; compounds for control of the retort atmosphere; and inert filler material. The reaction chamber (retort), charged with the proper materials, is sealed using a ceramic mixture having a softening temperature higher than the boiling temperature of the metallic reaction compounds present within the retort.

The entire pack system is heated to temperatures in the range between 1750°F and 2250°F for 4 to 8 h depending upon the desired composition and structure of the coatings. When, during the heating cycle, the temperature reaches 270°F the atmosphere-control compound (urea) melts, and on further heating vaporizes and decomposes to form biuret and ammonia. These gases expel air from the retort chamber and fill it with a reducing atmosphere which prevents oxidation of the components to be coated. Excess gases can escape through the sealing material, either when the seal is unmelted or after it becomes molten at higher temperatures. At reaction temperature (approximately 2000°F) the evolved gaseous reactants are held under pressure higher than atmospheric by the molten seal, but some excess gases can escape. When the reaction is complete and the retort is cooled, the seal solidifies and prevents the entrance of oxygen. The use of this kind of seal therefore prevents oxidation within the retort during the entire process cycle.

The procedure outlined above is used for single-cycle siliconizing with or without alloy additions, and for multicycle coating processes. The latter may involve a first cycle precoating followed either by a molybdenum alloy co-deposition diffusion cycle or by one or two metal-diffusion cycles. The nature of each coating is dependent upon the batch composition used.

EXPERIMENTAL PROCEDURE

It was imperative to examine all reasonably possible coating systems to insure that a good coating system would not be overlooked for subsequent process optimization stages of the research effort. The number of theoretically feasible coating systems is so

large that only a superficial examination of the process variables was possible for any given coating within the limited time allotted for process experimentation. For this reason all of the experimental coatings were made using one temperature, one batch process time, and one batch composition. The single batch composition for each coating was based on consideration of past experience, partial vapor pressure of the elements involved, density of the reactants, and the thermodynamics and kinetics of the particular process.

The experimental coating work was based on three major process concepts yielding three general types of coatings: (1) single-cycle co-deposition coatings; (2) multicycle co-deposition coatings; and (3) multicycle alternate layer coatings. All are diffusion coatings.

The first coating process concept involves single-cycle co-deposition of Si and an alloying element. Co-deposition and diffusion take place in one process cycle. Si powder is the chief metallic constituent of the reaction batch and alloying elements are present in much smaller amounts. Molybdenum silicides are the main coating constituents. The alloying elements investigated by the single cycle co-deposition process are the following: B, C, Co, Cr, Nb, Ta, V, W, and Zr. The ratio of silicon to alloying element in the coating is not known at this time but it is believed that the alloying elements are minor constituents.

The second coating concept involves a two-cycle process. The first cycle produces a chromium coating which is diffused into the substrate during the process cycle. The second cycle involves the co-deposition of silicon and another metal. Conversely, the first cycle may be the alloy co-deposition cycle, followed by a second cycle in which only one element is deposited. Diffusion occurs during all the process cycles so that complex composition gradients are established.

The coating systems for the multicycle co-deposition diffusion process investigated are as follows:

<i>First cycle</i>	<i>Second cycle</i>
Cr	Si + B
Cr	Si + C
Cr	Si + Co
Cr	Si + Mo*
Cr	Si + Ta
Cr	Si + V
Cr	Si + W
Cr	Si + Zr
Cr + Si	B
Cr + Si	C
Cr + Si	Co
Cr + Si	Mo
Cr + Si	Ta
Cr + Si	V
Cr + Si	W
Cr + Si	Zr

* PFR-4, a Pfadler proprietary coating.

The third coating process concept involves a multicycle alternate layer method in which, in separate cycles, alternate layers of chromium, silicon and alloying elements are deposited and diffusion-bonded to the substrate and to each other. The first cycle produces a chromium coating which is diffused into the substrate during the process

le. The second and third cycles produce a silicon alloy coating layer which, during process cycle, undergoes further diffusion to form a final coating very complex in composition. Thus, the chromium and the silicon or silicon and alloying elements deposited in the following cycles diffuse into each other and the chromium and molybdenum undergo further diffusion. Because of the complexity of these coating systems composition gradients that exist are not known.

The coating systems for the multicycle alternate layer process investigated are as follows:

<i>First cycle</i>	<i>Second cycle</i>	<i>Third cycle</i>
Cr	Si	B
Cr	B	Si
Cr	C	Si
Cr	Si	C
Cr	Co	Si
Cr	Si	Co
Cr	Ta	Si
Cr	Si	Ta
Cr	V	Si
Cr	Si	V
Cr	W	Si
Cr	Si	W
Cr	Zr	Si
Cr	Si	Zr
Cr	Si*	
Si	Cr	

* PFR-5, a Pfudler proprietary coating.

All experimental work to date has been performed using the Mo-0.5% Ti alloy as substrate since it is the only suitable base metal obtainable commercially. Thirty-mil thick sheet has been used for the bulk of the experimental work. Ten-mil thick sheets of the Mo-0.5% Ti alloy have also been obtained and will be coated. Close contact is being maintained with various mill producers to be sure that the latest developments in Mo alloys will be considered in the research program. Of particular interest is the TZM alloy.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

The several items of equipment needed to do the work were constructed at the Pfudler Research Laboratory. An instrumented oxyacetylene flame test facility has been set up. Oxygen and acetylene flow rates are regulated and metered to provide reasonably standard flame conditions. The oxygen-acetylene flow ratio has been maintained at 3 : 1 to provide a highly oxidizing flame. A test temperature of 3000°F has been used as an evaluation standard. This temperature was determined by optical pyrometer measurements using the conservative emissivity value of 1.0.

A typical Globar furnace used for sample coating is shown in Fig. 3. This is a 1.5 KVA furnace with 4 Globars (2 on each longitudinal vertical side), operating to 600°F, and having a usable retort volume $17 \times 7 \times 7$ in.³

A minimum bend radius test apparatus has been constructed (Fig. 4). The test is designed to evaluate the coated composite with respect to room temperature ductility

or formability. Sheet samples are bent around a die having a known nose radius. A series of dies of successively smaller radius are used until fracture of the coating occurs. The largest die has a radius of 0.75 in. and the smallest has a knife edge. The smallest die which does not produce failure determines the minimum bend radius. A female die having an included angle of 75° is used in conjunction with a hydraulic



Fig. 3. 12.5 KVA globar furnace.

jack to bend the sample around the radius. A known pressure, determined by a gage, is used on each sample. In this manner each sample is bent around a certain radius through a 105° angle with a specific maximum pressure. A thin rubber sheet is placed on each side of the sample during testing to avoid compression damage to the coating.

For performance evaluation one to four samples were tested for ductility in the bend test apparatus and for oxidation resistance at 3000°F in excess oxygen in the oxyacetylene torch facility. Bend tests were first conducted using $3/4\text{R}$ and $5/8\text{R}$ dies, but the relatively low ductility of most samples made necessary the adoption of the

R test coupled with additional performance data in order to evaluate the samples. Samples were bent to 250 p.s.i. around the $3/4$ R die. If a coating failed prior to 250 p.s.i. load, a percentage value of bend was established, i.e., a coating fracture at 200 p.s.i. could be considered to have reached 80% of the $3/4$ R bend. A minimum of two samples of each coating were so tested and ratings were assigned as follows: excellent—



Fig. 4. Bend test apparatus used to determine coating ductility.

one sample bent around $3/4$ R at 250 p.s.i. without failure; good—one sample bent around $3/4$ R at 250 p.s.i., one sample failed at a bend value greater than 50%; fair—one sample failed at a bend value greater than 50%; poor—both samples failed at a bend value less than 50%.

oxyacetylene torch test results were expressed as "time to failure" for the coatings. In these preliminary tests thermal cycling was not controlled and the number of thermal cycles ranged from 0 to 4. For the several coatings showing most promise

in the initial tests, more extensive bend and oxidation tests were conducted in order to reduce the number of coatings suitable for further exploration.

Upon completion of the first preliminary tests, the six coating systems showing the best behavior were further investigated. Additional samples were coated so that replicates were available. Oxyacetylene testing at 3000°F was repeated on duplicate samples using a thermal cycle of $\frac{1}{2}$ h at elevated temperature plus air blast cooling. This cycle was repeated until the sample failed. Further bend tests were carried out on duplicate samples. In those cases in which the coating was not visually damaged, bend tests were followed by oxyacetylene torch testing using the $\frac{1}{2}$ h thermal cycle.

RESULTS

Results of the initial evaluation of the single-cycle co-deposition coatings are included in Table II. It is evident that several of the coatings performed well in this test.

TABLE II
INITIAL EVALUATION OF SINGLE-CYCLE CO-DEPOSITION COATINGS

Coating	Oxyacetylene oxidation test life at 3000°F	Bend ductility: 0.032 in. thickness; 3/4R; 105° angle	Coating thickness (mils) and metallographic observations
Si + B	10 min	poor	1.5 — porous outer layer
Si + C	2 h 10 min	poor	2.8 — porous
Si + Nb	3 h 45 min	excellent	3.5 — not porous
Si + Co	2 h	fair	2.5 — porous
Si + Cr	1 h 9 min	good	2.5 — slightly porous
Si + Ta	6 h 40 min	good	4.5 — slightly porous
Si + V	1 h 30 min	fair	4.0 — very slightly porous
Si + W	1 h 30 min	fair	3.0 — very slightly porous
Si + Zr	25 min	excellent	4.0 — porous

Of particular interest are the Si + Nb, Si + Ta, Si + V and Si + W coatings. Of these, the Si + Ta and the Si + Nb are of most interest because of long oxidation test life and good ductility. The Si + C coating exhibited good oxidation test life but had poor ductility.

Results of the initial evaluation of the multicycle co-deposition coatings are shown in Table III. Once again, several of these coatings show promise although, in general, they are not as resistant to the 3000°F environment. Of particular interest are the Cr, Si + C; Cr, Si + Mo (PFR-4); and Cr, Si + V coatings, all of which endured about 2 h exposure at 3000°F. The data in Table III also indicate that those coatings involving a Cr - Si first layer followed by a single element second layer are in general less satisfactory than the coatings which consist of a chromium first layer followed by a co-deposited silicon + alloying element second layer.

Results of the initial evaluation of the multicycle alternate layer coatings are shown in Table IV. The performance of coatings based on this process concept was generally poor, the only exception being the Cr, Si system which had been investigated previously in this laboratory, and which has been designated as Pfaudler PFR-5. In most of the 3-cycle processes some recrystallization of the substrate occurred. This accounts for the uniformly poor room temperature ductility of these composites.

TABLE III

INITIAL EVALUATION OF MULTICYCLE CO-DEPOSITION COATINGS

Coating	Oxyacetylene oxidation test life at 3000°F	Bend ductility: 0.032 in. thickness; 3/4R· 105° angle	Coating thickness (mils) and metallographic observations
Si + B	1 h 55 min	fair	2.5 — porous
Si + C	2 h 10 min	good	3.0 — slightly porous
Si + Co	45 min	fair	2.5 — very slightly porous
Si + Mo ^a	2 h	good	1.0 — not porous
Si + Ta	1 h 40 min	fair	2.5 — slightly porous
Si + V	2 h 5 min	fair	4.0 — slightly porous
Si + W	1 h 30 min	good	3.0 — very slightly porous
Si + Zr	15 min	good	2.5 — porous
+ Si, B	50 min	fair	2.0 — porous
+ Si, C	1 min	fair	2.5 — very porous
+ Si, Co ^b	5 min	fair	3.5 — very porous
+ Si, Mo	28 min	fair	3.0 — very slightly porous
+ Si, Ta	33 min	poor	1.5 — very slightly porous
+ Si, V	2 min	fair	2.5 — very porous
+ Si, W	1 min	poor	3.0 — very porous
+ Si, Zr	45 min	poor	2.3 — slightly porous

FR-4.
tested at 2750°F.

TABLE IV

INITIAL EVALUATION OF MULTICYCLE ALTERNATE LAYER COATINGS

Coatings	Oxyacetylene oxidation test life at 3000°F	Bend ductility: 0.032 in. thickness; 3/4R; 105° angle	Coating thickness (mils) and metallographic observations
Si, B	42 min	good	1.5 — not porous
B, Si	38 min	poor	2.0 — not porous
Si, C	41 min	poor	2.0 — porous inner layer
C, Si	1 h 18 min	poor	3.0 — not porous
Si, Co	15 min	poor	1.5 — very slightly porous
Co, Si	1 h	poor	3.5 — slightly porous
Si, Ta	13 min	poor	2.5 — very porous
Ta, Si	33 min	poor	4.0 — porous inner layer
Si, V	15 min	poor	2.0 — slightly porous
V, Si	1 h 43 min	poor	3.8 — not porous
Si, W	17 min	poor	2.5 — slightly porous
W, Si	52 min	poor	3.8 — not porous
Si, Zr	13 min	poor	2.5 — porous outer layer
Zr, Si	1 h 2 min	poor	2.8 — porous
Si*	3 h 25 min	good	4.0 — not porous
Cr	1 h	fair	4.0 — porous

PFR-5

From the above review, which has been based primarily on oxyacetylene torch oxidation test results, a fairly large number of coatings appeared to be candidates for process variable study and ultimate optimization. Since a large number of coatings could not be investigated to this extent, significant parameters had to be intensively evaluated in order to select the one or two coating systems best suited for the study of process variables. The limitations of time and the need for a practical coating

prevented the detailed investigation which many of these promising coating systems richly deserved. The necessarily imposed experimental limitations of one process temperature, one batch process time, and one batch composition may have obscured some coating systems, but it appeared that sufficient information was available for a wise selection for process variable study and optimization.

When the initial screening tests recorded in Tables II, III and IV had been completed, additional oxidation and ductility tests were made on duplicate samples of several coatings. This resulted in the selection of six coatings for more intensive evaluation. New coated samples were made (replicates) using the same processing as in the initial experiments, and the samples subjected to evaluation.

Oxidation resistance re-evaluation was carried out on these replicate samples using a somewhat more severe test in that $\frac{1}{2}$ h thermal cycles were employed with an air blast (thermal shock) cooling ending each cycle. Ductility tests were repeated in duplicate on the new samples using the bend test apparatus. In those cases in which bending around a $3/4$ R die did not produce cracking, cyclic oxidation tests were performed subsequent to the bend test.

TABLE V
EVALUATION OF SELECTED COATINGS

Coating	Cyclic oxyacet. oxidation test life at 3000°F	Number of $\frac{1}{2}$ h thermal cycles ^a	Bend ductility: 0.032 in. thickness; $3/4$ R; 195° angle; 250 p.s.i.	Post-bending oxyacet. oxidation test life at 3000°F	Coating thickness (mils) and metallographic observations
Si + Nb	3 h 45 min	7	excellent	1 h 53 min	3.5 — not porous
	3 h 38 min	7		1 h 30 min	
Si + Ta	4 h 10 min	8	fair	not tested	4.5 — slightly porous
	4 h 5 min	8			
Si + V	3 h 20 min	6	excellent	1 h 35 min	4.0 — very slightly
	4 h 35 min	9		1 h 47 min	porous
Si + W	4 h 50 min	9	good	58 min	3.0 — very slightly
	4 h 53 min	9			porous
Cr, Si + Mo (PFR-4)	1 h 43 min	3	poor	not tested	1.0 — not porous
Cr, Si (PFR-5)	2 h 45 min	5	fair	not tested	4.0 — not porous

^a Thermal shock air blast at end of each cycle.

The results of the evaluation of the six replicated coatings are shown in Table V. Four of the single-cycle co-deposited coatings, one of the multicycle co-deposition coatings (PFR-4), and one of the multicycle alternate layer coatings (PFR-5) were tested. Cross-section photomicrographs of these coatings are shown in Figs. 5-10. Completely adequate mounting procedures had not been developed at the time some of these samples were photographed so that the Si + Nb and Si + Ta coatings (Figs. 7 and 8) exhibit cracking which is not representative of the as-coated samples. The dark bands at the upper sides of the coatings shown in Figs. 7 and 9 are caused by imperfect adherence of the sample mounting material to the outer coating surface.

All of the coatings performed adequately in the oxyacetylene torch testing but the



Fig. 5. Si + V coating on Mo: $\text{NaOH-K}_3\text{Fe(CN)}_6\text{-H}_2\text{O}$ etch. (250 $\times$)

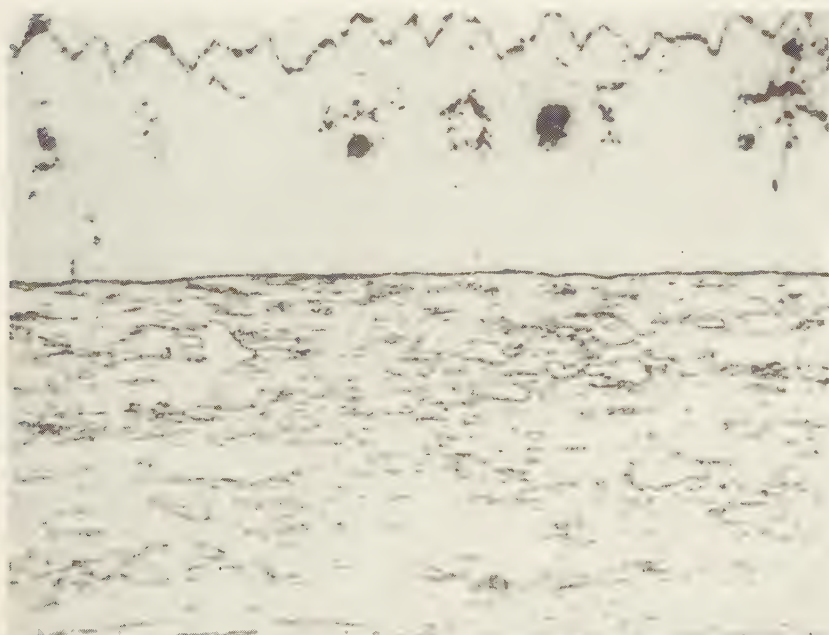


Fig. 6. Si + W coating on Mo: $\text{NaOH-K}_3\text{Fe(CN)}_6\text{-H}_2\text{O}$ etch. (250 $\times$)

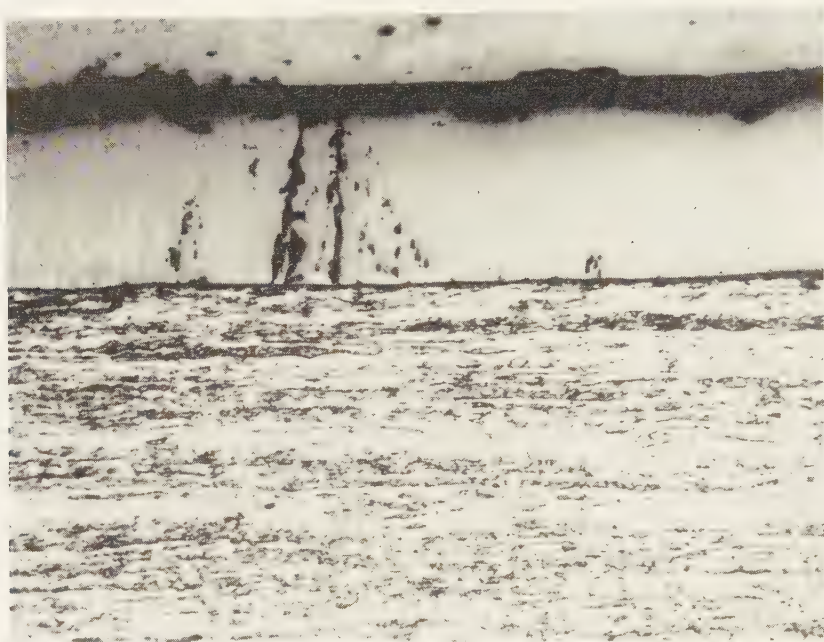


Fig. 7. Si + Nb coating on Mo: NaOH- $K_3Fe(CN)_6$ -H₂O etch. (250 $\times$)



Fig. 8. Si + Ta coating on Mo: NaOH- $K_3Fe(CN)_6$ -H₂O etch. (250 $\times$)



Fig. 9. Cr, Si + Mo (PFR-4) coating on Mo: NaOH- $\text{K}_4\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ etch. (250 $\times$)

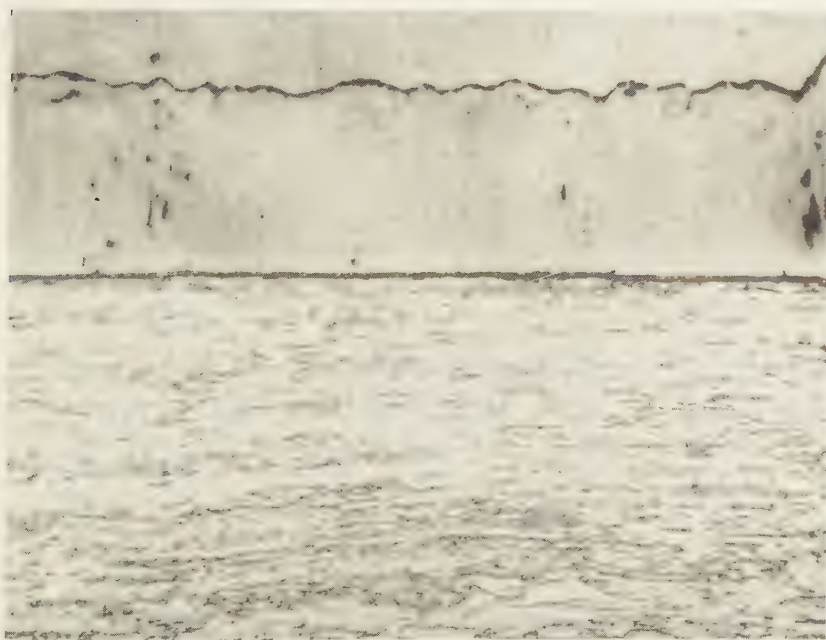


Fig. 10. Cr, Si (PFR-5) coating on Mo: NaOH- $\text{K}_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ etch. (250 $\times$)

oxidation life of the coatings was in some cases considerably different from that obtained in the initial tests (Tables II, III and IV). For example, the Si + Ta coating life was 6 h 40 min in the initial tests and 4 h 10 min in the replicate test. This would seem to be in accordance with the increased severity of the cyclic test used in the replicate testing. On the other hand the Si + V and Si + W coating exhibited far better oxidation life in the more severe replicate tests than was observed in the initial evaluation.

A similar pattern of results is evident for the ductility evaluation. Table V shows that the Si + V and Si + W replicate samples exhibited much greater bend ductility than had been noted in initial valuation and, on the other hand, the ductility of the the Si + Ta coating was less in the replicate tests.

The significant observation to be drawn from the above results is the need for variable identification and study in the two basic coatings systems, the single-cycle co-deposition, and the multicycle co-deposition or alternate layer system. Consistent or statistically significant results for oxidation resistance and ductility must be obtained for each coating composition in order that a specific coating composition can be chosen for studying other variables of the process.

CONCLUSION

The experimental work completed to date indicates that two coating concepts are worthy of further consideration. The first of these is a single-cycle co-deposition type of coating exemplified by the Si + Ta, Si + Nb, or Si + V systems. The second type of coating is a multi-cycle process involving alternate layers of elements such as Cr, Si (PFR-5) coating.

It is evident that a large number of coating compositions cannot be handled while conducting a proper process variable study. A specific coating composition cannot be selected for intensive variable study, however, without more knowledge regarding the effects of the various alloy compositions. Accordingly, a further study of co-deposition alloy additions in the single-cycle process and a study of the alternate layer (Cr, Si) process is to be undertaken to establish more firmly the effectiveness of the alloy additions (Ta, Nb, W and V) and to establish statistically reliable data upon which to base the selection of a single coating system for process variable study.

Following the completion of the above study, one coating system (involving one pack composition) will be selected for intensive investigation with regard to process and performance variables. Process variables to be considered include time of processing, processing cycle, temperature of process, variations within the pack composition, pack particle size and shape, and substrate precoating and post coating treatments. The performance characteristics to be evaluated include coating thickness, substrate-coating thickness ratios, ductility, oxidation resistance, thermal shock resistance, and effects of the coating on the mechanical properties of the substrate.

A complete understanding of the process variables of an optimized coating system should result in the availability of the reliable and reproducible coating required for advanced USAF aerospace vehicles.

ACKNOWLEDGEMENT

The work here reported was conducted as part of a project sponsored by the Air Research and Development Command of The United States Air Force.

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THE EQUILIBRIUM DIAGRAM OF THE SYSTEM
MOLYBDENUM-RUTHENIUM

E. ANDERSON AND W. HUME-ROTHERY

Department of Metallurgy, Parks Road, Oxford (Great Britain)

(Received September 2nd, 1960)

SUMMARY

The equilibrium diagram of the system molybdenum-ruthenium has been determined for temperatures above 1450°C. Molybdenum dissolves about 30.5 at.% Ru at high temperatures and the solubility diminishes quickly as the temperature falls. Ruthenium dissolves 51 at.% Mo at high temperatures and the solubility diminishes slowly with falling temperature. The sigma phase exists in the region of 37.0 ± 1 at.% Ru and is formed by a peritectoid reaction slightly below the 1945°C eutectic horizontal between the solid solutions in molybdenum and ruthenium. The lattice spacings of the different phases have been measured, and the V.P. hardness numbers were determined for alloys in the "as-sintered" state prepared by powder methods.

INTRODUCTION

There appears to be no published work on the constitution of molybdenum-ruthenium alloys above 1600°C. RAUB¹ made a systematic examination below this temperature, and showed that the solid solubility of ruthenium in molybdenum was very small, although the solubility of molybdenum in ruthenium increased with rising temperature to 35 at.% at 1600°C. RAUB claimed the existence of an intermediate phase Ru_3Mo_5 (37.5 at.% Ru), which was later shown by BLOOM² to possess the σ -type of structure. According to BLOOM the σ -phase exists over a narrow range of composition in the region of 30 at.% Ru, although GREENFIELD AND BECK³ claimed that the composition was about 40 at.% Ru. All these authors agreed that the σ -phase was stable only above about 1200°C.

The present paper describes a complete determination of the equilibrium diagram above 1450°C.

EXPERIMENTAL

Preparation of alloys

The alloys used in the present work were kindly prepared in the form of sintered buttons by Messrs. Murex Ltd., and the authors must express their thanks to Dr. G. L. MILLER for his care and attention. For the ruthenium, use was made of high purity metal, supplied by Messrs. Johnson, Matthey & Co., Ltd., which had been arc-melted in a vacuum in order to reduce the oxygen content. The ruthenium buttons were powdered and mixed with high purity molybdenum powder in which the principal impurities were O, 0.05%; C, 0.01%; Fe, 0.005%; and 0.03% lime, alkali metals, and silica. The mixed powders were cold pressed at 30 tons/sq. in., and sintered in hydrogen at temperatures between 1700° and 1800°C.

Liquidus and solidus determinations

The liquidus curves were determined by the quenching and microscopical method described by HAWORTH AND HUME-ROTHERY⁴. For temperatures up to 2300°C the specimens were heated in zirconia crucibles, whilst thoria crucibles were used for higher temperatures. All experiments were carried out in an atmosphere of argon at a pressure of 15–40 cm of mercury. Figs. 1 and 2 show a typical temperature bracket for an alloy containing 40.5 at. % ruthenium.



Fig. 1. Alloy Mo-40.5 at. % Ru. Quenched from above the liquidus. ($\times 100$)



Fig. 2. Alloy Mo-40.5 at. % Ru. Quenched from below the liquidus. ($\times 100$)

The solidus curves were determined by the conventional method of quenching and microscopical examination, the specimen being heated at the final temperature for 20 min before quenching. The same method was used for the determination of the solid solubility curves, for which the times of annealing were of the order 3-5 h, whilst additional results were obtained by lattice spacing measurements of quenched powders.

Etching technique

For alloys containing the Mo-rich solid solutions, satisfactory results were obtained with a solution containing 9 g sodium hydroxide and 2.5 g potassium ferricyanide dissolved in 380 ml of water. The times of etching varied from 30 sec to 1 h. The ruthenium-rich alloys were etched electrolytically using a solution of 200 ml of 20% aqueous hydrochloric acid and 1-2 ml hydrogen peroxide. With both these reagents, the intermediate σ -phase was unattacked.

X-ray methods

Phases were also identified by a simple method in which a small lump was broken off the specimen used for microscopical examination, and exposed in a Hilger 9 cm camera using a microfocus beam of Cu $K\alpha$ radiation. The lattice spacings of molybdenum-rich solid solutions were determined by the back reflection method used by FAWCOTT⁵. For the remaining phases, lattice spacings were measured by conventional powder methods using a 19 cm Unicam camera. All specimens were strain-annealed after powdering, and Cu $K\alpha$ and Cr $K\alpha$ radiations were used for the ruthenium solid solution and σ -phase alloys respectively.

EXPERIMENTAL RESULTS

Liquidus and solidus curves

The liquidus/solidus relations are of the simple eutectic type, and the results obtained are shown in Fig. 3. The freezing point of ruthenium was determined as $1310 \pm 20^\circ\text{C}$. This is lower than the estimated value of $2400-2500^\circ\text{C}$ given in reference books⁶⁻⁸ but in reasonable agreement with BAIRD's⁹ value of 2250°C . The eutectic point lies at $1945 \pm 10^\circ\text{C}$, and corresponds to the following reaction: liquid (41.6 at.% Ru) $\rightleftharpoons$ α Mo (30.5 at.% Ru) + α Ru (49 at.% Ru).

Terminal solid solutions

The solid solubility of ruthenium in molybdenum diminishes rapidly with temperature, and is about 13 at.% at 1500°C . The solid solution in ruthenium also becomes more restricted with falling temperature, but the change is not nearly so great.

The σ -phase

In the as-sintered condition, alloys in the composition range 35.0-39.5 at.% Ru contained 3 phases and were thus not in equilibrium. After annealing at the temperatures shown in Fig. 3, alloys containing 35.65 and 38.7 at.% Ru were 2-phase, and consisted of σ with small amounts of the molybdenum-rich and ruthenium-rich solid solutions respectively. The composition range of the σ -phase is thus narrow and cannot exceed the limits 37.0 ± 1 at.% Ru. These limits include the composition Mo_5Ru_3

suggested by RAUB¹, and disprove the results of both BLOOM² and GREENFIELD AND BECK³.

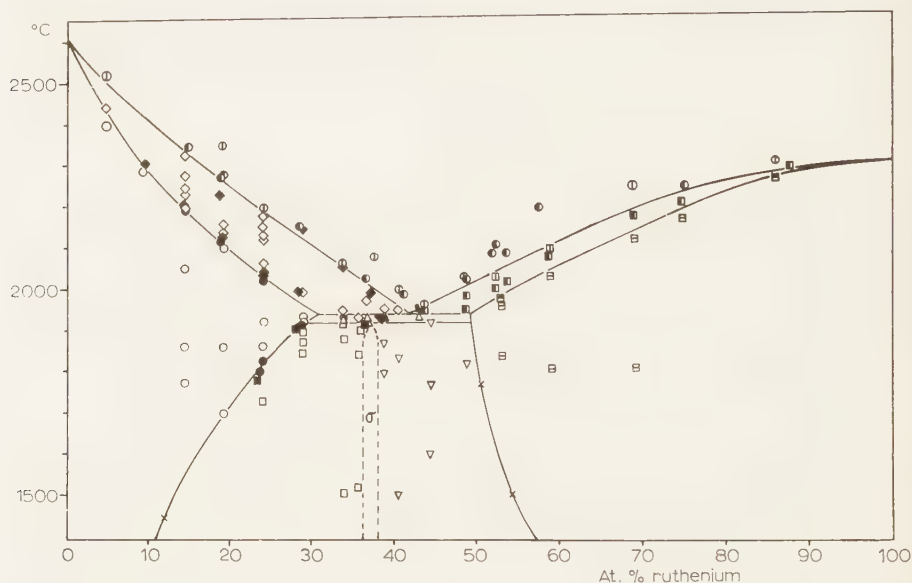


Fig. 3. Molybdenum-ruthenium equilibrium diagram. $\times$ refer to X-ray points. The full points refer to specimens analysed after the experiments. For the open points, the compositions are either taken to be the same as the analytical values for another specimen of the same bar, or are the synthetic values: $\circ$, α -Mo; $\odot$, quenched liquid; $\diamond$, α -Mo + liquid; $\square$, α -Mo + σ ; $\boxplus$, α -Ru; $\boxminus$, α -Ru + liquid; $\diamond$, α -Ru + σ ; $\triangle$, α -Mo + α -Ru.

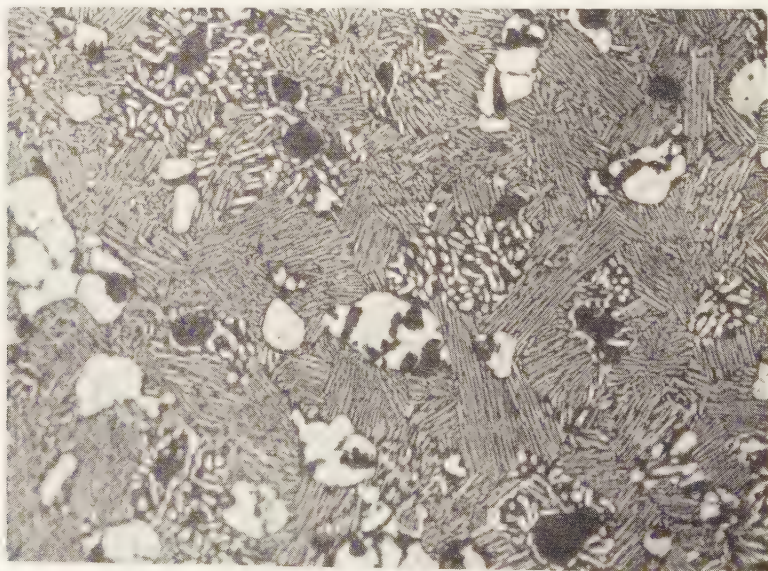


Fig. 4. Alloy Mo-38.25 at.% Ru. Quenched from 1936°C. ($\times 100$)

In the absence of any evidence, previous workers have assumed that the σ -phase

formed by a peritectic reaction, but the present work indicates a peritectoid horizontal at about $1920 \pm 10^\circ\text{C}$. The evidence for this is first that the alloys containing 15, 36.5, and 38.25 at.% Ru when quenched from between 1920 and 1945°C consisted of (α Ru + α Mo) with no indication of the σ X-ray diffraction patterns. These alloys also showed the curious microstructure of Fig. 4 which could be reconciled with a peritectoid decomposition of the σ -phase, but would not agree with a peritectic diagram. The structure of Fig. 4 is in fact very like that given by McQUILLEN¹⁰ for silver-titanium alloys in which the " Ag_3Ti " phase undergoes a peritectoid decomposition.

The σ -phase was found to persist in alloys which were cooled from 1900° to 1150°C for 24 h.

The lattice spacings of the σ -phase are shown in Table I. For the a spacings the result for the alloy containing 37.49 at.% Ru is slightly out of sequence. For the c spacings and the axial ratios the values change systematically with the variation of composition, and this indicates a very slight range of composition for the σ -phase.

TABLE I

LATTICE SPACINGS OF THE SIGMA PHASE IN THE MOLYBDENUM-RUTHENIUM SYSTEM

All the σ -phase specimens were heat treated at 1700°C for 2 h. Cr $K\alpha$ radiation was employed and the exposures taken between 20 and 23°C . The σ -phase X-ray specimens were analysed. The error in c/a was 0.0001, and ± 0.0004 kX in the a spacing.

At. % Ru	c/a	$a(\text{kX})$	$c(\text{kX})$
34.0 (α Mo + σ)	0.5161	9.5377	4.9224
35.15	0.5161	9.5380	4.9226
36.50	0.5162	9.5376	4.9233
37.49	0.5163	9.5382	4.9246

The lattice spacings of the terminal solid solutions

The lattice spacings of the solid solution of ruthenium in molybdenum are shown in Table II, and are plotted graphically in Fig. 5, together with the values previously

TABLE II

LATTICE SPACING RESULTS FOR THE MOLYBDENUM-RICH SOLID SOLUTION CORRECTED TO 20°C

All the specimens were analysed for ruthenium. The estimated error in the spacing values was ± 0.0002 kX.

At. % Ru	Camera	Radiation	Heat treatment	$a(\text{kX})$
Pure Mo	Unicam 19 cm	Cu $K\alpha$	$1850^\circ\text{C}/1$ h	3.1404
4.70	Back reflection	Mo $K\alpha$	$1890^\circ\text{C}/1$ h	3.1352
9.50	Back reflection	Mo $K\alpha$	$1860^\circ\text{C}/2\frac{1}{2}$ h	3.1294
14.27	Back reflection	Mo $K\alpha$	$1820^\circ\text{C}/1$ h	3.1240
18.68	Back reflection	Mo $K\alpha$	$1855^\circ\text{C}/2$ h	3.1189
18.68	Back reflection	Mo $K\alpha$	$1855^\circ\text{C}/2$ h	3.1187
19.10	Unicam 19 cm	Cu $K\alpha$	$1384^\circ\text{C}/5$ h	3.1272
(2-phase)				

found for solutions of rhodium and palladium⁴. For a given atomic percentage of solute the lattice contraction becomes more marked on passing from Pd $\rightarrow$ Rh $\rightarrow$ Ru, and thus runs parallel to the atomic diameters of the solutes.

The a and c spacings, and the axial ratios c/a for the solid solution of molybdenum in ruthenium are shown in Table III and Fig. 6. Both a and c spacings are expanded by the addition of molybdenum, and the a vs. composition curve is a straight line. The axial ratio increases with increasing percentage of molybdenum, and there is a kink in the curve connecting axial ratio with composition, which indicates a much more rapid increase after about 10 at. %.

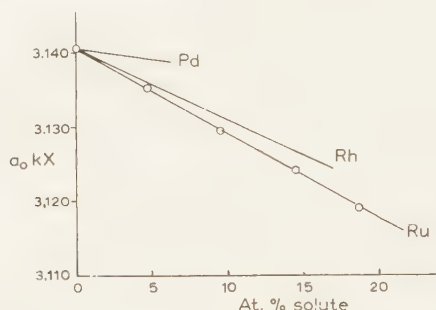


Fig. 5. Lattice parameter relations for the molybdenum-rich solid solutions in the molybdenum-ruthenium, molybdenum-rhodium and molybdenum-palladium systems.

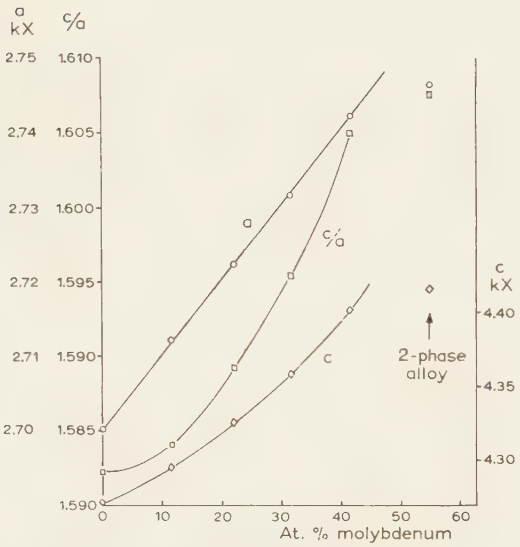
TABLE III

LATTICE SPACING RESULTS FOR THE RUTHENIUM-RICH SOLID SOLUTION CORRECTED TO 20°C

All the X-ray specimens were analysed for ruthenium. The a spacing should be accurate to ± 0.0002 kX and c/a to ± 0.0001 .

At. % Mo	Heat treatment	c/a	a (kX)	c (kX)
Pure Ru	1800°C/1 h	1.5823	2.7002	4.2725
11.55	1868°C/3 h	1.5841	2.7121	4.2962
22.2	1765°C/6 h	1.5893	2.7223	4.3266
31.4	1888°C/2 h	1.5955	2.7317	4.3584
41.45	1877°C/2 h	1.6050	2.7423	4.4014
55.0	1773°C/2½ h	1.6112	2.7506	4.4318
(2-phase)				
54.9	1508°C/2 h	1.6078	2.7466	4.4160
(2-phase)				

Fig. 7 shows the relation between the mean volume per atom and the composition. In this figure it is assumed that the unit cell of the σ -phase contains the normal number (30) of atoms. The expansion of the unit cell of ruthenium by the solution of molybdenum is almost exactly that expected from a linear relation between the atomic volumes of the two elements (*i.e.*, a "volume Vegard's Law"), but the contraction of the lattice of molybdenum by solution of ruthenium is not so great as would be expected from a linear law. The formation of the σ -phase is accompanied by an expansion relative to a linear law.



6. Lattice spacing/composition relations for the ruthenium-rich solid solution in the molybdenum-ruthenium system.

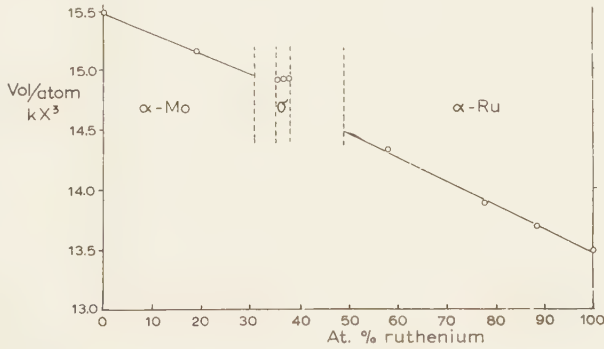
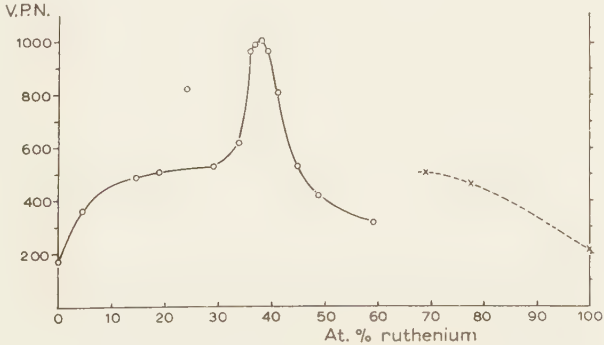


Fig. 7. Atomic volume relations in the molybdenum-ruthenium system.



8. Vickers Pyramid hardness data for molybdenum-ruthenium alloys: $\circ$, sintered; $\times$, arc-melted.

The hardness of the sintered alloys

Fig. 8 shows V.P. hardness for the alloys in the as-sintered state provided by Messrs. Murex Ltd. The hardness of molybdenum is increased by the addition of ruthenium, and the very high value for the alloy containing 24 at. % Ru is due to a precipitate of the σ -phase in the grains of the molybdenum solid solution. The σ -phase itself is very hard, but brittle. In the as-sintered state the alloys of high ruthenium content were too porous for the results to be of value. A few alloys were prepared in an argon arc furnace and the hardness numbers of these in the annealed state are included in Fig. 8, and show that the hardness of ruthenium is increased by the addition of molybdenum.

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DIRECT CASTING OF URANIUM MONOCARBIDE REACTOR FUEL ELEMENTS

W. M. PHILLIPS, W. CHUBB AND E. L. FOSTER

Battelle Memorial Institute, Columbus, Ohio (U.S.A.)

(Received August 17th, 1960)

SUMMARY

Procedures for preparing uranium carbide cast shapes with densities in excess of 98% of theoretical are described. In the first method, drop casting, uranium and crushed carbon are melted six times in a special carbon-electrode arc furnace in which the charge can be turned over after each 30-sec melting cycle. The carbon content of the 100 g UC button is homogeneous and controlled to ± 0.1 wt. % carbon. This button is then cast in a second arc furnace into a graphite thimble mold. Castings up to 5/8-in. in diameter by 3 in. long weighing 200 g can be made. In the second technique, charges of UC up to 8 kg are skull melted under vacuum or inert gas in a carbon-electrode arc furnace. While good quality castings round, square, and hexagonal in cross section can be made and are homogeneous to ± 0.1 wt. % carbon, variation of carbon contents from melt to melt of ± 0.3 wt. % carbon have been noted.

For economical nuclear power depends upon fuel-cycle costs, any advance in fuel technology is of great importance. Therefore, the development of a material which would be an improvement over existing fuels is of interest to all potential producers of nuclear electrical power. Uranium monocarbide appears to be such a fuel. It has high thermal conductivity (almost that of metallic uranium), a melting point of about 2400°C, a theoretical uranium density of 13 g/cm³, and, on the basis of early data, good radiation-stability characteristics¹⁻³. In addition, the feasibility of preparing UC shapes by casting techniques has been fully demonstrated. The fact that a refractory hard metal like UC can be produced by pyrometallurgical techniques establishes an interest in the technique for the production of other fairly high melting compounds. With this in mind the arc-casting methods used successfully for UC are discussed briefly in the following paragraphs.

Numerous ways for preparing uranium monocarbide have been explored. LITZ and LITZ⁴ reacted powdered uranium at 650°C with a stream of methane to produce uranium hydride. As the temperature was increased the hydride reacted with the methane to produce uranium monocarbide. In other work, molten uranium has been successfully reacted with graphite to produce uranium monocarbide^{5,6}. Direct combination of powdered graphite and uranium as well as uranium oxide also has been successfully used⁷.

Shapes of UC powder have been produced by pre-forming with a temporary wax binder. Compacting and sintering of the UC powder has produced densities of 11.4 g/cm³ or an effective uranium density of 11.4 g/cm³, which exceeds the uranium content of 100% dense UO₂. To date, however, the most promising method of producing sound, dense shapes is by inert-electrode arc melting followed by casting. Two

casting processes, drop casting and skull-type arc melting, have exhibited capability to produce sound dense shapes.

Drop casting is an ideal method for preparing small shapes (up to about diameter 5/8 in., length 3 in.) of UC. In the method employed, a charge of freshly pickled as-reduced uranium and crushed spectrographic-grade carbon is placed in the crucible

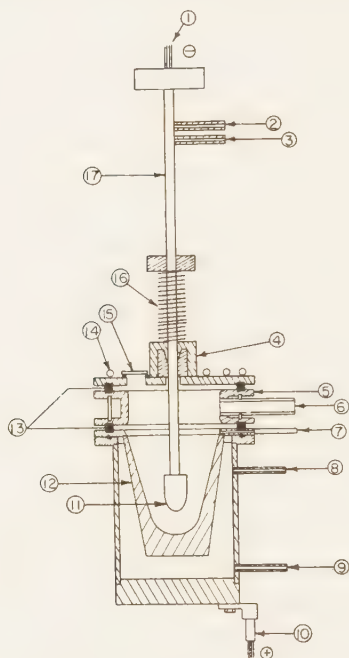


Fig. 1. Charge-flipping arc furnace: 1, — to rectifiers; 2, water outlet; 3, water inlet; 4, Wilson seal; 5, water-cooled spacer; 6, main vacuum line; 7, gas inlet; 8, water outlet; 9, water inlet; 10, + to rectifiers; 11, graphite electrode; 12, Cu crucible; 13, neoprene gas-kets; 14, Cu tubing for water cooling; 15, sight glass; 16, compression spring; 17, water-cooled electrode.

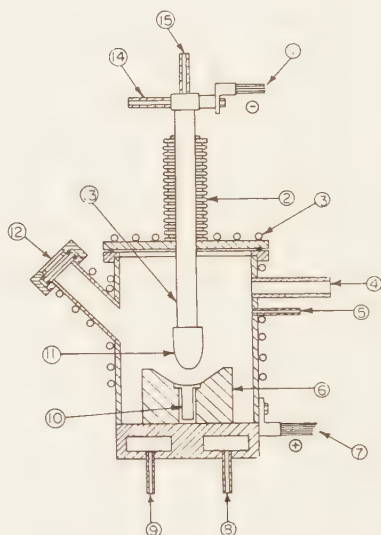


Fig. 2. Laboratory-type arc furnace with graphite thimble mold and Cu mold support: 1, — to rectifiers; 2, brass bellows; 3, Cu tubing for water cooling; 4, main vacuum line; 5, gas inlet; 6, Cu mold support; 7, + to rectifiers; 8, water inlet; 9, water outlet; 10, graphite thimble mold; 11, graphite electrode tip; 12, sight glass; 13, water-cooled electrode; 14, water outlet; 15, water inlet.

of the furnace similar to the one shown in cross-section in Fig. 1. In this design, the charge can be flipped over after each melt without opening the furnace by merely striking a blow on the bottom of the furnace shell. The furnace chamber is evacuated, and a helium atmosphere of 10 to 20 in. of Hg absolute is bled into the furnace.

The melting process consists of initially striking the arc by means of a high-voltage arc starter and raising the current to 500 A to obtain a molten pool. A non-consumable, carbon-tip electrode is used since the only contaminant from such an electrode is carbon. Carbon pick-up from the electrode is reduced by rounding the carbon tip and limiting the melting time to 30 sec. Use of six 30 sec melts, with the button flipped after each melt, produces consistently homogeneous buttons weighing 100 g.

Cylinders of uranium monocarbide are cast from these pre-alloyed buttons in the

laboratory-type arc furnace shown in Fig. 2. The steps involved in the process of drop casting are discussed in detail below.

- (1) The required amount of material is placed over the opening of the mold.
- (2) The furnace is evacuated and back-filled with helium to a pressure of approximately 20 in. of Hg absolute.
- (3) An arc is struck and the current increased to obtain a small molten pool beneath the arc. The arc is then rotated in concentric circles over the surface of the charge, which preheats the mold and consolidates a multibutton charge into one button.
- (4) The amperage is increased still further until the charge is melted through, allowing the molten UC to drop into the graphite mold.

The castings prepared by this method are well-formed and have a smooth surface with a metallic luster. The densities obtained are 98% of theoretical or better, and there is no observable porosity in the microstructures. However, the behavior of the material during casting is not unlike a metal, and, therefore, the castings may show some defects such as centerline shrink cavities, cracks, and areas of surface roughness. The possibility of these defects occurring increases with increased casting size, but this can be counteracted by proper mold design and melting procedure.

It has been observed that an outgassed, heated mold will improve surface quality and almost completely eliminate cracking. The elimination of cracking by using a heated mold has been attributed to lower cooling rates. The rate of cooling has also been reduced by using thin mold walls (1/16 in.) and by suspending the thin molds in the hearth by the outer edge of the mold lip, and by evacuating the furnace immediately after the arc is extinguished allowing the casting to cool in vacuum. The finished castings are removed from the furnace after a 10–15 min cooling period. The copper hearth, a casting prior to removal from a graphite mold, a sectioned mold, and casting are shown in Fig. 3.

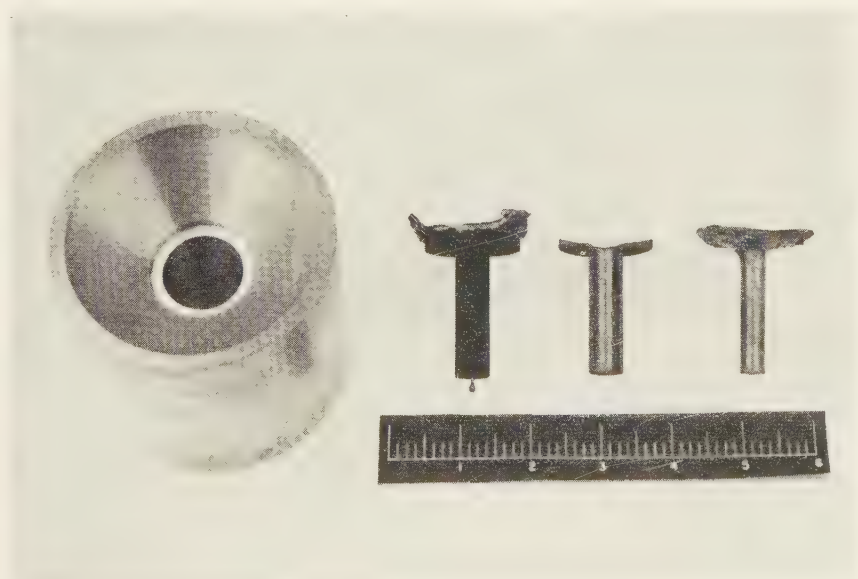


Fig. 3. Hearth, mold, and casting from the laboratory-type arc furnace.

Since a 3/8 in. diameter by 1 $\frac{3}{4}$ in. casting weighs approximately 50 g and is made from a 100 g button, the effect of remelting the skull from previous castings has been studied. As shown by Table I the carbon and nitrogen content is only slightly changed by remelting previously alloyed material. The analyses given in Table I also are indicative of the composition and homogeneity control that is possible in this process.

The impurity content of the castings produced by this drop-casting process is reduced with the exception of oxygen and nitrogen. Hydrogen is reduced from 10 p.p.m. to a value of about 6 p.p.m. The amount of calcium, iron, magnesium, nickel and silicon

TABLE I
EFFECT OF REMELTING ON CARBON AND NITROGEN CONTENT OF UC

Charge	Position of sample	Analysis (wt. %)	
		Carbon	Nitrogen
Virgin U + C	Skull	4.93	0.015
	Casting top	4.95	0.018
	Casting bottom	4.94	0.015
Virgin U + C	Skull	4.99	0.024
	Casting top	4.93	0.026
	Casting bottom	4.98	0.024
Remelted UC	Skull	4.92	0.021
	Casting top	4.99	0.020
	Casting bottom	4.95	0.022
Remelted UC	Skull	4.95	0.019
	Casting top	4.97	0.021
	Casting bottom	4.98	0.020

TABLE II
IMPURITY CONTENT OF UC PRODUCED BY DROP CASTING AND SKULL-TYPE ARC MELTING AND CASTING TECHNIQUES

Impurity	Drop-casting technique		Skull-melting technique		
	Total impurity in melt stock* for drop casting (p.p.m. in U)	Impurity in finished drop casting (p.p.m. in C)	Impurity in melt stock for skull melting (p.p.m.)		Impurity in finished skull casting (p.p.m. in UC)
			in C	in U	
Al	20	20	ND**	40	20
B	1	2	ND	1	1
Ca	15	ND	700	20	20
Cu	5	5	ND	10	5
Cr	6	ND	ND	—	ND
Fe	125	50	20	80	15
H	10	6	—	2	<1
Mg	1	ND	1	10	2
Mo	5	5	ND	40	5
N	40	170	—	100	50
Ni	20	15	ND	30	2
O	10	110	—	10	100
Si	40	10	50	300	40
Ti	ND	ND	200	20	ND
V	ND	ND	100	—	ND

* In drop casting, spectrographic-grade carbon is used and no significant quantities of impurities are present.

** ND = not detected.

also lowered slightly. This reduction is illustrated by the typical analysis shown in table II.

Drop casting can produce specimens of consistently high quality suitable for studies of the properties of uranium carbide. However, in order to produce the amounts of fuel needed for fueling a reactor, a melting and casting technique to produce larger castings is necessary. Inert-electrode skull-type arc melting was selected as the most feasible method of obtaining the high temperatures and temperature control required, while maintaining the purity obtained by drop casting. As in drop casting, a carbon electrode tip and water-cooled copper crucible are used. The skull is built up within the crucible by a series of melts of uranium + carbon charges which solidify along the crucible walls to maintain electrical contact while providing some degree of thermal insulation.

Skull melting has been carried out under helium, argon and vacuum. Satisfactory temperature control and an adequate molten pool are obtained under all conditions. A 2 kg charge can be melted in 5 min at 3500 A and 18–22 V under helium or argon. Under vacuum, 15–20 min is required to outgas and produce a molten pool of similar size at a pressure of $5\ \mu$ at the same power input. The melting technique evolved employs a 8 kg charge melted for 30 min under a vacuum of less than $5\ \mu$.

As shown in the photograph of the furnace interior (Fig. 4) the molds and an induction coil to heat the molds are attached to the crucible to facilitate tilt pouring. Power is supplied to the induction coil through bus bars and two knife switches which open when the crucible is tipped.

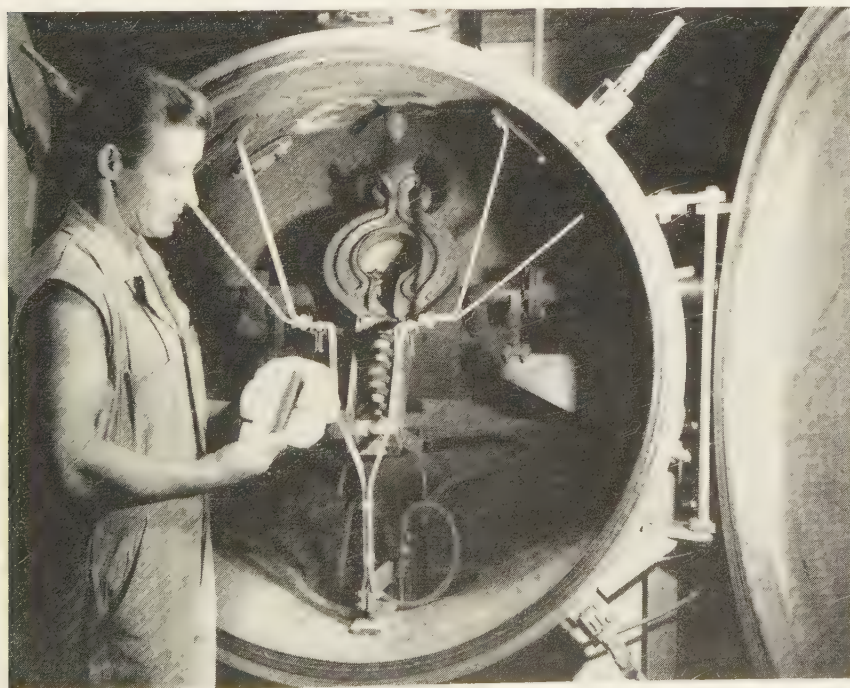


Fig. 4. Interior of arc skull furnace showing mold, mold heating coil, and crucible arrangement.

Castings of UC have frequently been found to contain internal cracks if cast into an unheated mold. This cracking diminishes with increasing mold temperature and has not been observed in castings poured into a mold heated above 2000°F. Cracking also appears to be related to the atmosphere used during melting and casting. Castings made under an argon or helium atmosphere are cracked more frequently



Fig. 5. Three of the UC shapes produced by inert-electrode arc skull melting: left, 1 in. diameter by 8 in. cylinder; center, $1\frac{1}{2}$ in. by $1\frac{1}{2}$ in. by 8 in. square; right, 1 in. by 8 in. hexagonal prism.

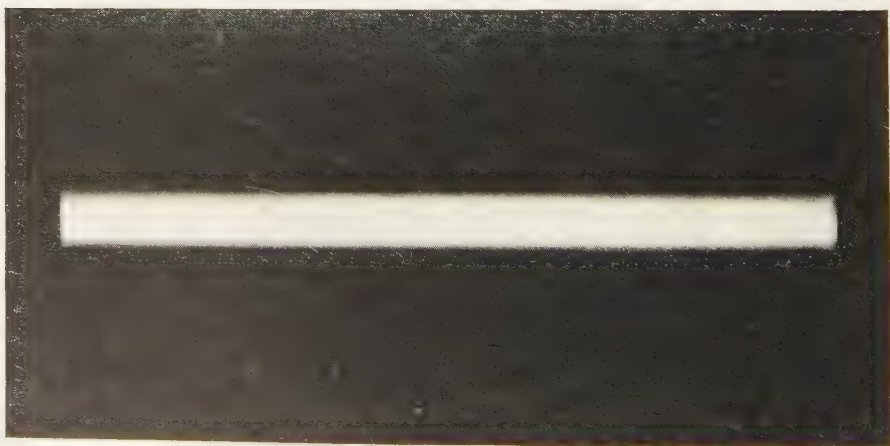


Fig. 6. Radiograph of a typical $\frac{5}{8}$ in. diameter by 8 in. long UC specimen.

in those produced under vacuum. This has been attributed to the higher cooling rate in an atmosphere as compared with that in a vacuum.

Shapes which have been cast by the process are shown in Fig. 5. As can be seen from the photograph, all corners are sharp and the surfaces are good. Radiography (a typical radiograph is reproduced in Fig. 6) and sectioning indicate that the castings are free of cracks. These data, combined with the observed good fluidity of the melt during the time of pouring, indicated that more intricate shapes than the right prisms shown can be cast.

Control of impurities is very good as indicated by Table II, showing the impurity content of two melts made from low-purity uranium and commercial purity electric-furnace electrode carbon. Carbon content of skull-melted materials has been controlled within ± 0.1 wt. % along the length of an 8 in. casting. Control from melt to melt present is within ± 0.3 wt. % carbon. This variation is caused by inhomogeneities in the skull and erosion of the graphite electrode tip which varies with the amount of outgassing of the melt. Current work indicates that the variation of carbon content from melt to melt decreases as the number of melts made in the same skull increases. Outgassing of the melt aggravates the erosion of the graphite electrode in two ways: (1) by reaction with the furnace atmosphere; (2) by splatter which drips back into the charge. Further improvement in carbon control is expected with improvements in charging and melting practice.

These studies have demonstrated that uranium monocarbide can be prepared routinely by drop-casting techniques in sizes up to 5-8 in. diameter and 3 in. lengths with densities greater than 98% of theoretical, and that castings of up to 8 kg with densities greater than 98% of theoretical can be prepared by skull-type arc-melting techniques. Carbon content within a single casting is being held to within ± 0.1 wt. %, and within ± 0.3 wt. % from melt to melt. The use of a dynamic vacuum during inert-electrode arc melting greatly reduces the impurity content of castings made from low cost commercial-purity materials. It is believed that the techniques developed and described here can be scaled up to a production operation with little difficulty. It is believed that this arc-casting technique is amenable to the production of other high-melting compounds in sound shapes of high density.

ACKNOWLEDGEMENT

Acknowledgement is given to the US-AEC and the Atomic International Division of North American Aviation Company, for their interest in and support of this work. The work was performed under AEC contract W-7405-eng-92.

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SOME STUDIES ON INORGANIC PEROXY-ACIDS II. PEROXY COMPLEXES OF TITANIUM

E. RICHARDSON

Dept. of Chemistry, Whitehaven College of Further Education, Cumberland (Great Britain)

(Received September 16th, 1960)

SUMMARY

The reaction of hydrogen peroxide with potassium titanyl oxalate in water and various acids has been investigated using conductometric, potentiometric, ion migration spectrophotometric and ion exchange techniques. The hydrogen peroxide forms an anionic complex with the titanyl oxalate ion which is in equilibrium in mineral acid solution with other neutral and anionic titanium species. Ion exchange studies have also been made on the interaction of titanium sulphate with hydrogen peroxide.

INTRODUCTION

Much confusion exists in the literature concerning the peroxy compounds of titanium even though these compounds form the basis of the standard method of colorimetric estimation¹⁻⁷. This confusion is due in part to the difficulty of preparing pure standard titanium salts which can be recrystallised from aqueous solution. Other errors have arisen from the use of a single experimental technique. It was thought of interest, therefore, to investigate the reaction of hydrogen peroxide with potassium titanyl oxalate (which can be obtained in a pure state), particularly in the presence of mineral acids, using the widest variety of applicable experimental techniques.

EXPERIMENTAL

Standard titanium solutions (0.02 *M*) were prepared by dissolving AnalaR $K_2TiO(C_2O_4)_2 \cdot 2 H_2O$ (99.5%) in distilled water. Oxalate-free titanium solutions were prepared by dissolving $K_2TiO(C_2O_4)_2 \cdot 2 H_2O$ in concentrated sulphuric acid, boiling until all the oxalate was destroyed, then diluting to the required volume. Peroxide solutions were prepared from unstabilised hydrogen peroxide (20 volume) kindly supplied by Laporte Chemicals Ltd., and standardised against acid potassium permanganate. All other chemicals were of AnalaR grade where available.

Ion exchange experiments were performed using resin samples (chromatographic grade) which had been regenerated several times, then washed free from all reagent before use.

Paper electrophoresis studies were made using a Shandon Vertical Type tank with a Vokam constant voltage unit normally operating at 300 V. Ion migration studies were made in a specially prepared small Hittorf apparatus with anode and cathode compartments of capacity ~ 11 ml. Conductance measurements were made on a Pye Conductance Bridge with a cell of constant 1.38.

pH measurements were made on a Cambridge pH-meter with a glass-calomel electrode unit standardised at pH 4.00 using 0.05 *M* potassium hydrogen phthalate. Spectrophotometric measurements were made on either a Hilger Uvispek or a Unicam S.P. 600 with cells as indicated.

RESULTS AND DISCUSSION

Equilibria in solutions of potassium peroxy titanyle oxalate

Addition of hydrogen peroxide to potassium titanyle oxalate produces a yellow coloration quite different from that produced by peroxy titanium solutions in sulphuric acid solution. The absorption spectrum of these systems is shown in Fig. 1

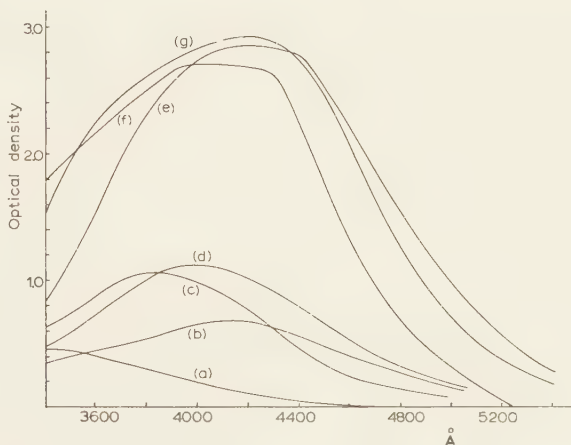


Fig. 1. Absorption spectra of peroxy titanium complexes: (a) $\text{K}_2\text{TiO}(\text{Ox})_2$ (0.00133 *M*), H_2O_2 (0.00066 *M*), NaAc (0.05 *M*), pH 5.9; (b) $\text{K}_2\text{TiO}(\text{SO}_4)_2$ (0.002 *M*), H_2O_2 (0.002 *M*), H_2SO_4 (0.4 *N*); (c) $\text{K}_2\text{TiO}(\text{Ox})_2$ (0.002 *M*), H_2O_2 (0.002 *M*); (d) electrolysis cell, +ve compt; (e) $\text{K}_2\text{TiO}(\text{Ox})_2$ (0.009 *M*), H_2O_2 (0.01 *M*), HCl (5 *N*); (f) $\text{K}_2\text{TiO}(\text{Ox})_2$ (0.009 *M*), H_2O_2 (0.01 *M*); (g) electrolysis cell, —ve compt; cell 0.5 cm.

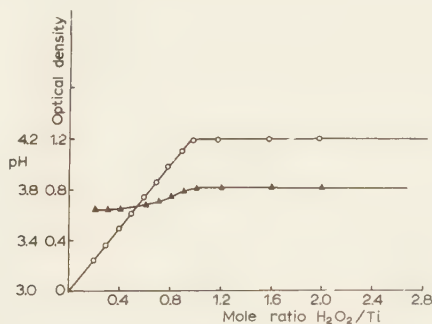


Fig. 2. Mole ratio method: $\text{K}_2\text{TiO}(\text{Ox})_2$, 0.0133 *M*; H_2O_2 , 0–0.0266 *M*; 1 cm cell; 4900 Å; O, optical density; ▲, pH.

The titanium complex in oxalate solution has a maximum absorption at 3800 Å, peroxy titanyle sulphate of similar concentration at 4075 Å. The wavelength at both maxima varies with concentration, the latter much more than the former.

The empirical formula of the complex in oxalate solution was determined using the Mole Ratio method (Fig. 2) and JOB's method of continuous variations. In the latter method the optical density of solutions prepared from 0.02 M $K_2TiO(Ox)_2$ and H_2O_2 was measured directly and after 1-10 and 1-20 dilution at various wave lengths from 3700-4500 Å. A 1 : 1 complex was formed in all cases.

The charge on the complex was determined by paper electrophoresis and ion migration studies. The migration of titanyl oxalate ions and titanyl oxalate ions in hydrogen peroxide is shown in Fig. 3. From this figure it is clear that negatively

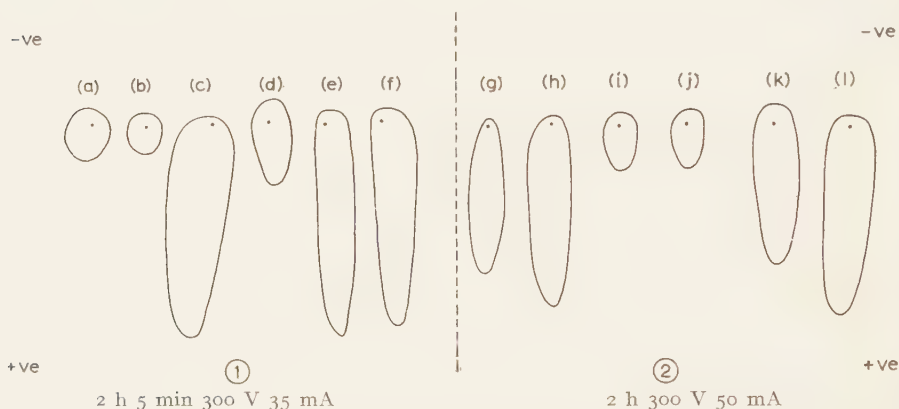
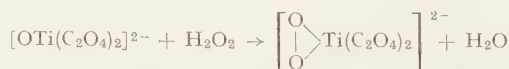


Fig. 3. Paper electrophoresis: developed with 20 vol. H_2O_2 ; electrolyte $\sim 0.01 M$ $HClO_4$; (a) 0.01 M $K_2TiO(Ox)_2$, 0.5 N HCl ; (b) 0.01 M $K_2TiO(Ox)_2$, 0.5 N H_2SO_4 ; (c) sat. $K_2TiO(Ox)_2$; (d) 0.01 M $K_2TiO(Ox)_2$, 5.5 N HCl ; (e) 0.01 M $K_2TiO(Ox)_2$; (f) 0.01 M $K_2TiO(Ox)_2$, 0.5 N HAc ; (g) 0.01 M $K_2TiO(Ox)_2$; (h) 0.01 M $K_2TiO(Ox)_2$, 0.01 M H_2O_2 ; (i) 0.01 M $K_2TiO(Ox)_2$, 0.01 M H_2O_2 , 0.5 N HCl ; (j) 0.01 M $K_2TiO(Ox)_2$, 0.01 M H_2O_2 , 0.5 N HCl ; (k) 0.01 M $K_2TiO(Ox)_2$, 0.5 N HCl ; (l) 0.01 M $K_2TiO(Ox)_2$, 0.1 M H_2O_2 , 0.5 N HCl .

charged ions, which migrate at similar rates are formed in both instances. Presumably, therefore, the hydrogen peroxide forms a complex with the titanyl oxalate ion, not the titanyl ion, similar in some respects to the complex peroxy titanium sulphates.



This experiment was repeated at several dilutions with similar results. Electrolysis of potassium peroxy titanyl oxalate in a small Hittorf tube for 100 min at 2 mA and 120 V completely decolorised the cathode compartment, confirming the anionic nature of the peroxy complex.

Further evidence for the peroxy titanyl oxalate ion was obtained from conductance studies. In 0.01 M solution the conductance of the potassium peroxy titanyl oxalate is greater than that of the titanyl oxalate solution. In more dilute solution the reverse is true (Fig. 4). The former result is best explained in terms of a greater degree of dissociation of the stronger peroxy salt in concentrated solution. On dilution, however, this is more than compensated by the partial decomposition of the complex titanyl oxalate ion in the absence of the stabilising influence of the peroxide group.

Addition of acetic acid has no effect on the composition or the absorption spectrum

the complex, nor has a mixture of sodium acetate and acetic acid. Addition of sodium acetate to produce a pH of 5.8–6.0, however, shifted the composition of the complex from a Ti:active O ratio of 1 : 1 to 2 : 1. This effect is presumably due to a change in the nature of the potassium peroxy titanyl oxalate at this pH value. The

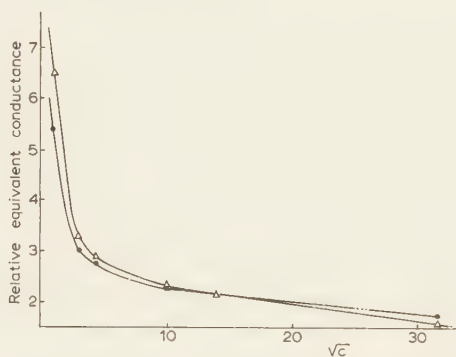


Fig. 4. Equivalent conductance of $K_2TiO(Ox)_2$ in H_2O_2 : Δ , $K_2TiO(Ox)_2$; $\bullet$, $K_2TiO(Ox)_2 + H_2O_2$; c is expressed in arbitrary units in which $c = 1000 = 0.0133 M$ (conductance $= 1.75 \cdot 10^{-3}$ mho at $24.2^\circ C$). Relative equivalent conductance is conductance $\times$ dilution; cell constant, 1.38.

absorption spectrum at pH 6.0 is shifted towards the shorter wavelengths. It is important to note, however, that both in this solution and in later studies using peroxy titanium sulphate solutions a precipitate ultimately formed at pH values > 4 . BABKO AND VOLKOVA⁵ claim that although the colour fades in peroxy titanium solutions in mineral acids at pH > 3 no precipitation occurs even at pH values > 5 . The decoloration is claimed by these workers to be due to formation of a stable colourless complex. Addition of hydrogen fluoride bleaches the yellow colour of the peroxy titanyl oxalate. In solutions of peroxy titanyl sulphate this bleaching is believed to be due to the formation of the colourless TiF_6^{2-} ion. Bleaching of the colour is not complete in peroxy titanyl oxalate solution. Addition of other mineral acids to the oxalate solution produces a reddish coloration with a spectrum similar to that of peroxy titanyl sulphate. At constant pH all of the anions investigated appeared to have a similar effect (Table I) and a continuous variation study showed that a 1 : 1 complex (Ti:active O) was still formed in each case. The theoretical significance of this is discussed later.

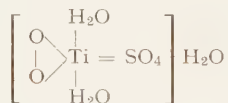
TABLE I

THE EFFECT OF VARIOUS MINERAL ACIDS ON THE OPTICAL DENSITY OF POTASSIUM PEROXY TITANYL OXALATE SOLUTION

Solutions prepared from 2 ml 0.01 M $K_2TiO(Ox)_2 \cdot H_2O_2$ + mineral acid to pH 1.7 when diluted to 50 ml total

Acid	Optical density		
	4800 Å	4500 Å	4000 Å
HCl	0.085	0.185	0.340
HNO ₃	0.085	0.185	0.340
H ₂ SO ₄	0.085	0.180	0.330
HClO ₄	0.085	0.185	0.340

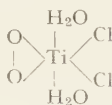
Further information on the species present in peroxy titanium solutions was obtained by electrolysis of 0.01 *M* potassium peroxy titanyl oxalate in 0.5 *N* HCl for 80 min at 6 V and 5.3 mA in a small Hittorf tube. A marked difference in colour was produced in the two compartments. Analysis, however, showed a uniform titanium content. The solution in the cathode compartment had the characteristic spectrum of acidified titanium solutions, the anode compartment that of peroxy titanyl oxalate. Two interpretations of this phenomena are possible, either separation of a positively charged peroxy titanium species and a negatively charged peroxy titanyl oxalate ion has occurred at an equal rate or most of the titanium has remained stationary under these conditions (0.5 *N* HCl) and the colour changes are due to changes in the hydrogen ion and oxalate ion (formed by partial decomposition of the peroxy titanyl oxalate) concentrations produced by migration of these ions. Due to the small changes involved and the difficult analytical conditions it is not easy to distinguish between these two suggestions although other evidence favours the latter. Paper electrophoresis studies show that no migration of the titanium occurs in $K_2TiO(C_2O_4)_2$ or $K_2TiO_2(C_2O_4)_2$ 0.5 *N* with respect to either HCl, H_2SO_4 , HNO_3 or $HClO_4$. It is also unlikely that many free peroxy titanyl oxalate ions exist since ionisation of the acid (shown later in this work to be capable of existence) is presumably inhibited by the high hydrogen ion concentration. Moreover, PATEL AND MOHAN⁷ in a recent spectrophotometric and migration study suggest that in sulphuric acid solution the peroxy titanyl sulphate complex is uncharged



while BEUKENKAMP AND HERRINGTON⁸ in a recent ion exchange study on the nature of Ti^{4+} in sulphuric acid suggest that in 0.5–1.5 *M* H_2SO_4 more than 60% of the titanium exists as uncharged $Ti(OH)_3HSO_4$. Thus although the peroxy titanyl oxalate ion is negatively charged it appears from these studies that an uncharged species possibly containing the anion of the acid occurs in some mineral acid solutions, in marked contrast to the suggestions of JAHR² and later GASTINGER³ who believed the colour in peroxy titanium solutions to be due to the peroxy titanyl ion $[TiO_2aq]^{2+}$. Since identical spectrophotometric results are obtained by acidification of potassium peroxy titanyl oxalate to pH 1.70 with HCl, HNO_3 , H_2SO_4 and $HClO_4$ (Table I), if the anion of the acid does enter the complex it has little effect on the absorbing group.

The equilibrium between the various species present in solution containing hydrochloric acid was examined further using ion exchange techniques at constant chloride concentration. Between pH values of 3.5–2 the titanium is exchanged completely on I.R.A. 400 in the chloride form. At pH values 2–1, up to 12% of the titanium passes through the column presumably either uncharged or positively charged. At pH values < 1 the percentage of titanium exchanged rapidly decreases. Only a small quantity of titanium (similar to that of a non-acidified solution) is retained on a similar column of ZeoKarb 225 in the hydrogen form when a 10 ml aliquot of 0.01 *M* peroxy titanyl oxalate 0.5 *N* with respect to HCl is passed through it. Presumably,

Therefore, under these conditions in HCl much of the peroxy titanium species is uncharged and exists probably as



similar to the sulphate complex suggested by PATEL AND MOHAN⁷ since it has been shown by the method of continuous variations to have a Ti:active O ratio of 1:1. Since the complex has not been isolated as a solid however, no definite evidence for the presence of the chloride within the molecule exists.

Equilibria in solutions of peroxy titanium sulphate

Since the conclusions of PATEL AND MOHAN⁷ on the species present in peroxy titanium sulphate solution were obtained only from spectrophotometric and ion migration studies it was thought of value to re-investigate the system using ion exchange techniques.

Oxalate free peroxy titanium sulphate solution was prepared by decomposing potassium titanyle oxalate with concentrated sulphuric acid, then adding the calculated quantity of hydrogen peroxide. Exchange of this solution with I.R.A. 400 in the sulphate form was then examined (Fig. 5). In both cases some of the titanium was

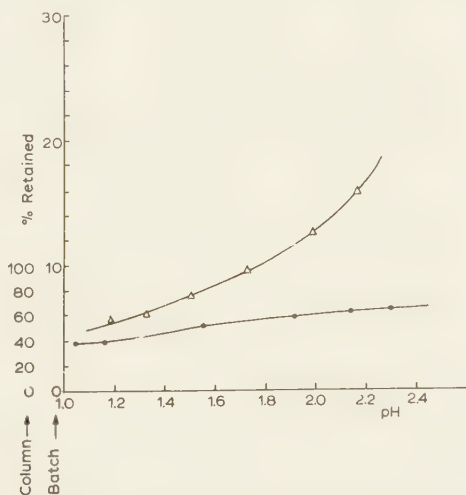
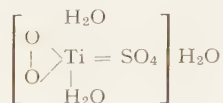


Fig. 5. Anion exchange studies on potassium peroxy titanium sulphate solution: (a) column studies $\bullet$, Ti (0.001 M), H_2SO_4 (0.18 N), KOH to produce pH values shown; column, 5 g I.R.A. 400 SO_4^{2-} ; exchange 10 ml sample; (b) batch studies Δ , 1 g I.R.A. 400 SO_4^{2-} + 25 ml of solutions above shaken 1 week. pH > 2.17, turbid solutions.

retained by the resin as a peroxy anion. The fraction retained increased with pH. It appears reasonable to suppose therefore that a peroxy ion of the type



originally suggested by SCHWARTZ¹ and later by SCHAEPI AND TREADWELL⁴ does exist in equilibrium with the uncharged peroxy compound



suggested by PATEL AND MOHAN⁷ and confirmed in the present study by paper electrophoresis techniques. The ion adsorbed certainly contains peroxide since the liquid obtained on regeneration of the column with 2 *N* H₂SO₄ has the characteristic colour of the peroxy titanyl complex. Moreover, BEUKENKAMP AND HERRINGTON⁸ have satisfactorily explained the equilibria in titanium sulphate solution in the absence of peroxide in terms of cationic species only.

Peroxy titanyl oxalic acid

It was not found possible to prepare the free peroxy titanyl oxalic acid by acidification of potassium peroxy titanyl oxalate solution since the characteristic coloration of peroxy titanyl sulphate was obtained. Free peroxy titanyl oxalic acid can, however,

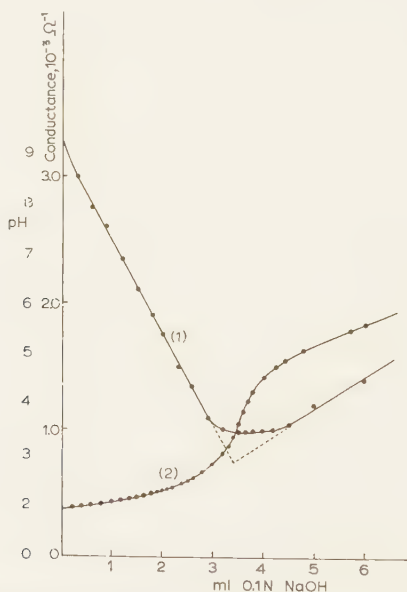


Fig. 6. Conductometric and pH titrations on peroxy titanyl oxalic acid; exchange 100 ml 0.01 *M* K₂TiO(Ox)₂ in 1 vol. H₂O₂ by 10 g column Zeokarb 225 H⁺; titration of 20 ml aliquots; (1) conductometric; (2) pH.

be prepared from potassium peroxy titanyl oxalate solution almost quantitatively by ion exchange using a column of Zeokarb 225. Only a small quantity of the titanium (~4%) is retained on the column. Typical conductometric and potentiometric titrations on the acid are shown in Fig. 6. The free acid is dibasic, both hydrogen atoms readily being replaced. Addition of a small quantity of HCl or H₂SO₄ again

produced the characteristic colour of peroxy titanyl sulphate but addition of NaCl or Na_2SO_4 had no immediate effect. Thus the colour is not due solely to the presence of anions of this type although it appears from the ease of preparation of peroxy titanyl oxalic acid by ion exchange, that their presence is a factor in inducing the formation of the second species.

The author wishes to thank Mr. J. G. FOSTER and Mr. T. HYDE who assisted with the preliminary spectrophotometric investigation.

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THE NIOBIUM-HYDROGEN SYSTEM

S. KOMJATHY*

International Business Machines Corp., Chicago, Ill. (U.S.A.)

(Received October 10th, 1960)

SUMMARY

Niobium-hydrogen equilibrium was studied in the temperature range 300°–1500°C between 0 and 760 mm Hg equilibrium H₂ pressure by the SIEVERTS technique. Continuous solid solution is formed in this range, which exhibits b.b.c. structure with lattice parameter increasing with increasing hydrogen content. The formation of the solid solution is exothermic; heat of solution increases with increasing hydrogen content.

Below 300°C, X-ray diffraction analysis and metallographic examination revealed the existence of a non-classical phase transformation, which is possibly martensitic or order-disorder type.

INTRODUCTION

Several investigations have been carried out to establish the niobium-hydrogen and niobium-deuterium equilibria¹⁻⁵. Recent interest in niobium for high-temperature and nuclear applications and the availability of higher purity niobium metal stimulated the revision of the earlier experimental data. The solubility of hydrogen in solid niobium has been repeatedly studied applying the SIEVERTS technique^{6,7}, the thermal balance⁸, X-ray diffraction analysis⁹⁻¹³, supplemented with metallographic examination of the alloys^{7,11}. Good agreement was indicated by these studies⁶⁻¹³ regarding the general behavior of the system. Deviations of the numerical values of the hydrogen solubility were attributed to variations in the purity of the niobium metal used. From the investigations carried out, from room temperature up to 1000°C and between 10 and 1000 mm Hg equilibrium hydrogen pressures, the following conclusions can be summarized.

The absorption of hydrogen by niobium resulted in exothermic formation of a single-phase solid solution in the temperature range 300° to 1000°C between compositions 0.0 to 0.85 atomic ratio N_H/N_{Nb} . The lattice parameter and heat of solution increased with increasing hydrogen concentration. The absorption obeyed SIEVERTS' law from 1000° down to about 600°C. From this temperature down to 300°C the system exhibited negative deviations from SIEVERTS' law, *i.e.*, at a given temperature, lower external hydrogen pressure resulted in higher solubility than could be expected theoretically. With decreasing temperature the deviations became more pronounced, suggesting some kind of transformation under 300°C temperature⁷. X-ray diffraction analysis and metallographic examination revealed the existence of a two-phase field

* Formerly Associate Metallurgist, Armour Research Foundation, Illinois Institute of Technology.

between compositions 0.09 to 0.68 atomic ratio N_H/N_{Nb} ^{7,9-13}. Below 300°C the b.c.c. single-phase solid solution splits into two b.c.c. phases differing only in lattice parameter; $a_0 = 3.301 \pm 0.002$ Å at $NbH_{0.09}$ (α) and 3.41 Å at $NbH_{0.68}$ (β). On further cooling, an orthorhombic distortion of the b.c.c. lattice of the β -phase was reported with parameters $a = 4.84$ Å, $b = 4.90$ Å, and $c = 3.45$ Å at $NbH_{\sim 0.7}$ ^{7,9-13}. The orthorhombic distortion reversibly diminishes on heating, and from about 100°C upwards the lattice is substantially cubic¹³. The change of the lattice parameters of a β -phase ($\alpha + \beta$) alloy was found to be anomalous and inconsistent with the existing concepts of a miscibility gap. The lattice parameters measured during heating of a β -phase alloy indicated stable phases corresponding to compositions within the miscibility gap¹³. On further heating at about 250°C, the two b.c.c. phases transformed into a b.c.c. single phase with lattice parameters corresponding to the hydrogen content of the alloy¹³. The anomalous characteristics of the transformation, the tilt appearance of the surface of quenched alloys and the morphology of the transformed structure suggested the possibility of martensitic transformation¹¹.

The scope of this research work was to study the niobium-hydrogen equilibrium between 300° and 1500°C and 0 to 760 mm Hg external hydrogen pressures by the EVERTS technique. The vapor pressure measurements were supplemented with room-temperature X-ray diffraction analysis and metallographic examination of the alloys.

EXPERIMENTAL MATERIALS AND METHODS

Electron-gun-refined niobium (supplied by E. I. du Pont de Nemours Company) was rolled into 1 mil thick foil and 0.05 in. diameter rod was used. Analysis of the rolled metal obtained by vacuum-fusion technique and semiquantitative spectrographic analysis is shown in Table I.

TABLE I
ANALYSIS OF NIOBIUM METAL

Element	p.p.m. by weight	Method and analyst
O ₂	400	Vacuum fusion by Chemical Research Services, Inc.
N ₂	40	
H ₂	<10	
Ta	100-1000	Semi-quantitative spectrographic analysis by Charles Kawin Co.
Mo	10-100	
Al	5-50	
Cu	5-50	
Ni	5-50	
Pb	5-50	
Si	5-50	
Sn	5-50	
V	5-50	
Bi	not detected	
Cd		
Co		
Cr		
Fe		
Mn		
Ti		
W		
Zn		

Pure hydrogen was obtained by the thermal dissociation of titanium hydride prepared from dry tank oxygen and titanium sponge.

A modified form of SIEVERTS apparatus was used for the experiments, which was described in detail elsewhere¹⁴. The niobium specimen was equilibrated with hydrogen in a quartz reaction vessel designed for this study. Two different reactors were constructed: one with molybdenum resistance internal heating and water-cooled walls for the temperature range 900° to 1500°C (Figs. 1(a) and (b)), the other with Ni-Cr resistance external heating for temperatures between 300° and 900°C (Figs. 2(a) and (b)).

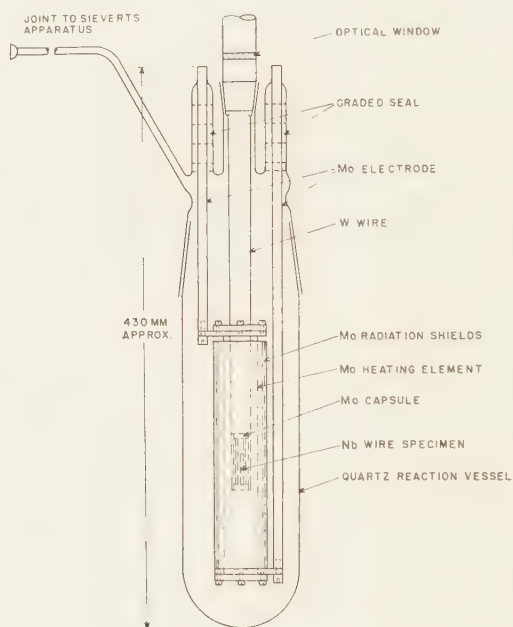


Fig. 1(a). Schematic diagram of the high-temperature reaction vessel.

The application of a separate high-temperature reactor with water-cooled walls is a necessity to avoid the contamination of the niobium specimen. At about 950°C the quartz starts to decompose, releasing oxygen. A piece of annealed niobium strip 0.03 in. thick (hardness 90 VPN) was heated at 1500°C for 5 h in the high-temperature reactor, which was previously evacuated to 10^{-6} mm Hg vacuum and closed off from the pumping system. The hardness of the metal did not change, indicating that no contamination occurred. An optical pyrometer was used for temperature measurement of the niobium specimen during the experimental runs. The effect of the optical window (Fig. 1(a)) on the temperature measurements was eliminated by temperature calibrations suggested in ref. 15. The error of the temperature measurements is estimated to be $\pm 5^\circ\text{C}$.

The temperature of the low-temperature reactor (Fig. 2(a) and (b)) was controlled with an automatic control device calibrated with temperature measurements of the reactor heat zone by a separate thermocouple. The error of the temperature control is estimated to be $\pm 1^\circ\text{C}$. Because of the special design of the low-temperature reactor, specimens could be quenched into water within 1-2 sec from the equilibrium temper-

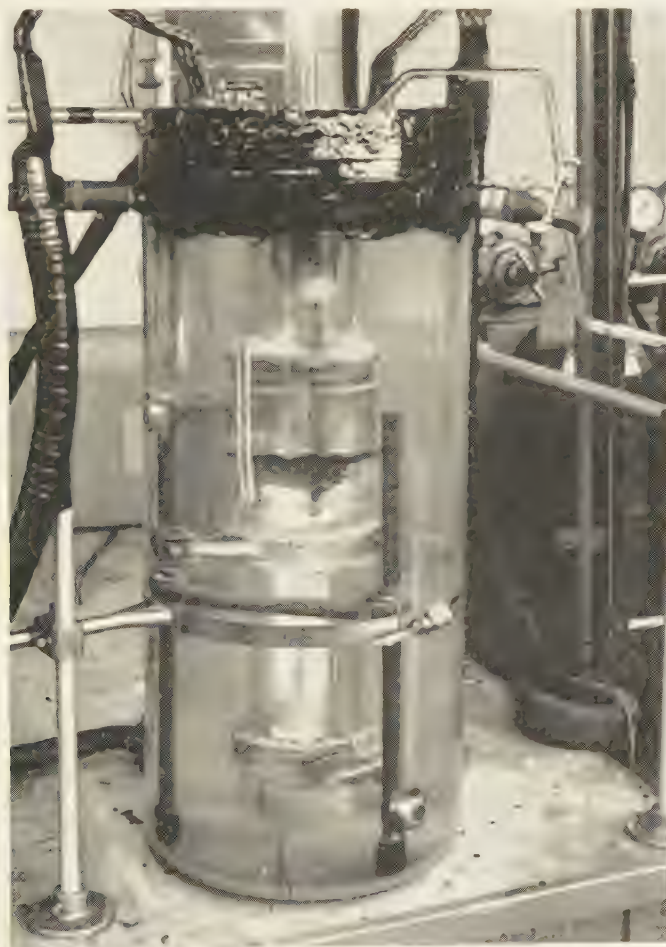


Fig. 1(b). High Temperature Reaction Vessel.

ture to provide samples for X-ray diffraction analysis and metallography. The high-speed quenching proved to be very efficient for retaining the equilibrium hydrogen composition of the alloy. Table II gives a comparison between the compositions calculated from vapor pressure measurements and vacuum fusion analysis of quenched specimens.

For the temperature range 900°–1500°C, specimens consisted of 13–15 g of niobium rod or foil. For temperatures 300°–900°C, 4–5 g of niobium foil exclusively was used because of time considerations. Above 600°C equilibrium was reached almost in-

TABLE II
HYDROGEN CONTENT OF QUENCHED Nb-H ALLOYS

Temperature before quenching (°C)	Hydrogen content (wt. %)	
	calculated	analysed by vacuum fusion
800	0.0568	0.0538
450	0.674	0.658

stantaneously. At lower temperatures the time requirements increased; at 300°C 4–5 h was needed to reach equilibrium. Prior to the experimental runs the niobium specimens were degassed in CCl₄, abraded with emery paper, etched in HNO₃–HF acid mixture and recrystallized at 1000°C for 1 h at 10^{–6} mm Hg.

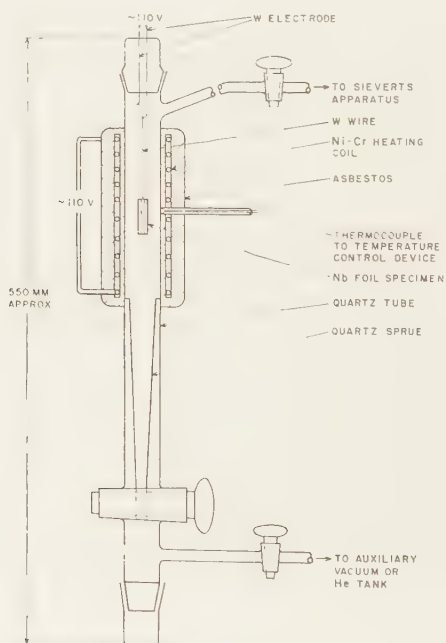


Fig. 2(a). Schematic diagram of the reaction vessel used in temperature range 300°–900°C.

Equilibrium data were obtained by adding successive portions of hydrogen gas into the reaction vessel isothermally — in 50°C increments from 300° to 700°C and in 100°C increments from 700° to 1500°C. Another procedure was to add a certain amount of hydrogen gas into the vessel at the desired temperature and, after equilibrium was reached, to change the temperature. The amount of hydrogen absorbed

the niobium metal was calculated in atomic ratio $N_{\text{H}}/N_{\text{Nb}}$ by the equation given in ref. 14. The possible relative error of the composition values was calculated to be 1% within the range of these experiments.

A Norelco powder camera and diffractometer was used for the X-ray diffraction analysis. The metallography and X-ray diffraction followed standard practice and need not be discussed.

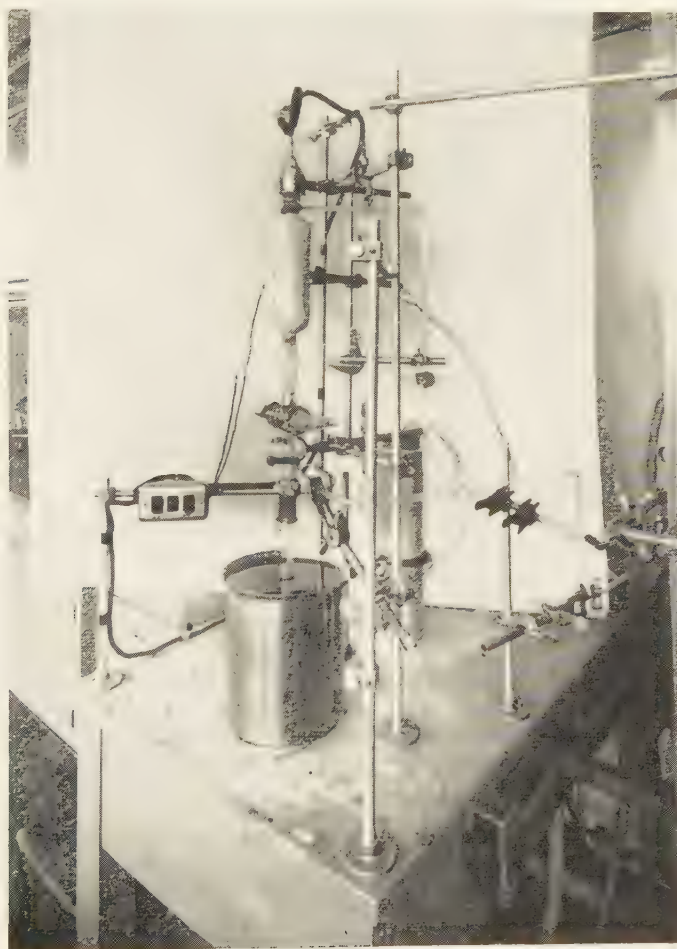


Fig. 2(b). Low-temperature reactor.

EXPERIMENTAL RESULTS AND THERMODYNAMIC DATA

According to SIEVERTS' law for the isothermal dissolution of hydrogen in niobium metal

$$N_{\text{H}} = \text{constant} \cdot \sqrt{P_{\text{H}_2}},$$

the atomic fraction of hydrogen in solid solution N_{H} is expected to vary linearly with

the square root of the equilibrium pressure of the molecular hydrogen P_{H_2} . Wherever this condition is satisfied, the gas-metal solid solution can be considered as a dilute solution of atomic hydrogen in niobium¹⁶.

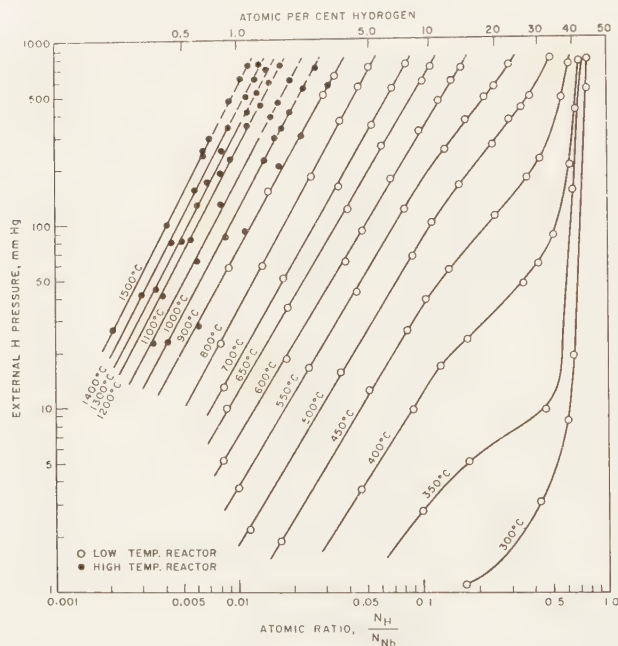


Fig. 3. Isotherms in system Nb-H: o, low-temp. reactor; ●, high-temp. reactor.

The results of the vapor-pressure measurements are presented in Figs. 3 and 4; P_{H_2} is plotted *versus* atomic ratio N_H/N_{Nb} in logarithmic scale (Fig. 3) and in linear scale (Fig. 4).

In the temperature range 900°–1500°C and above 300 mm Hg hydrogen pressures the isotherms slightly deviated from linearity on the logarithmic plot (Fig. 3). Because these data were obtained by using the high-temperature reaction vessel (Fig. 1(a) and (b)), it was suspected that the deviations were due to some occlusion of hydrogen by the molybdenum heating element. Blank runs were carried out without putting the niobium specimen into the reactor, and the hydrogen absorption of the molybdenum heating device was determined in the range 900°–1500°C. The measurements with niobium were corrected with the results of the blank runs so that the isotherms turned out to be straight lines in the entire pressure range. The corrected part of the isotherms is drawn by dashed lines in Fig. 3. The 900°C isotherm was also determined by using the low-temperature reactor, which was heated externally (Fig. 2(a) and (b)). The isotherm obtained is a straight line and shows good agreement with that obtained with the high-temperature reactor and corrected with blank run for pressures above 300 mm Hg.

The thermodynamic data, free energy, entropy, and heat of formation of solid solution were calculated from the experimental results of the vapor-pressure measurements obtained in the temperature range 400°–1000°C. The solubility values below 400°C were not used in the thermodynamic calculations because of the possible inaccuracy of these values due to the slow diffusion experienced at these temperatures.

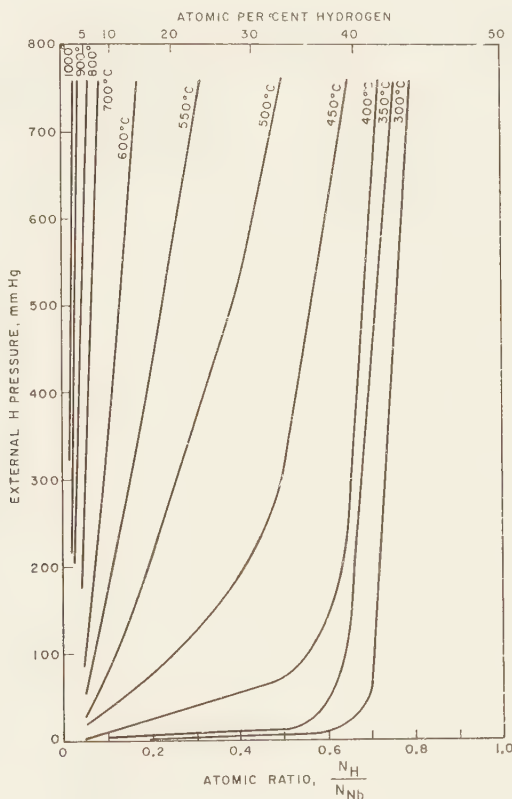


Fig. 4. Isotherms in system Nb-H.

The relative partial molal free energy of the dissolution of hydrogen $\bar{F}_H - F^\circ_{H_2}/2$ was calculated from the relationship:

$$\bar{F}_H - \frac{F^\circ_{H_2}}{2} = \frac{RT}{2} \ln P_{H_2}$$

where R is the gas constant and T is the absolute temperature of the absorption process. The integral free energy of formation ΔF_f of the niobium-hydrogen solid

solution per gram-atom of alloy was obtained by graphical integration of the corresponding GIBBS-DUHEM equation:

$$\Delta F_f = (1 - N_H) \int_0^{N_{Nb}} \left(\bar{F}_H - \frac{F_{H_2}^\circ}{2} \right) d\left(\frac{N_H}{N_{Nb}}\right)$$

The partial and integral molal entropies $\bar{S}_H - S_{H_2}^\circ/2$ and ΔS_f , respectively, were evaluated from the slope of plots $\bar{F}_H - F_{H_2}^\circ/2$ and ΔF_f versus temperature.

It was found that the entropy values were invariant with temperature but varied with the hydrogen concentration of the solid solution. The entropy values were combined with the corresponding free energy values to calculate the relative partial and the integral molal heat of solution, $\bar{H}_H - H_{H_2}^\circ/2$ and ΔH_f , respectively, according to the GIBBS-HELMHOLTZ equation,

$$\Delta F = \Delta H - T\Delta S,$$

which is valid for both partial and integral quantities.

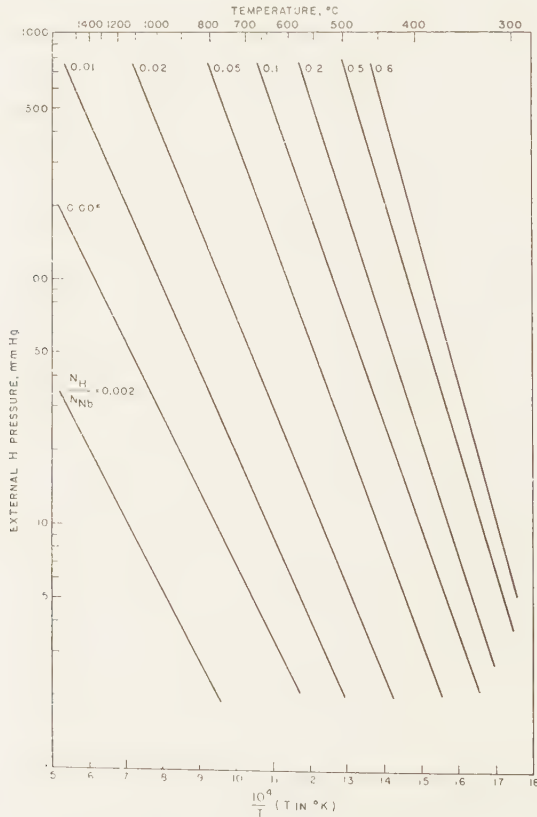


Fig. 5. Isoleths in system Nb-H.

The values ΔH_f and $\bar{H}_H - H^\circ_{H_2}/2$ were found to be independent of temperature, but increasing negative values were obtained with increasing solute concentration referring to the increasing exothermic character of the formation of niobium-hydrogen solid solution with increasing hydrogen content. This is also demonstrated in Fig. 5, which plot was prepared on the basis of the solubility data according to the equation:

$$P_{H_2} = \text{constant} \cdot \left(\frac{N_H}{N_{Nb}} \right)^2 \cdot e^{\frac{\Delta H_f}{RT}}$$

$\log P_{H_2}$ was plotted *versus* $1/T$ at constant concentrations. The slope of the lines yields ΔH_f , which is the partial relative molal heat of solution of molecular hydrogen.

Thermodynamic data are presented in Table III for 400°C at different solute compositions. The enthalpy and entropy values are naturally valid for other temperatures, considering the temperature independence observed.

TABLE III
THERMODYNAMIC DATA FOR Nb-H SOLID SOLUTIONS AT 400°C

Thermodynamic function	Atomic ratio N_H/N_{Nb}					
	0.05	0.1	0.2	0.3	0.4	0.5
ΔF_f (cal/g-atom) ^a	-240	-380	-570	-720	-820	-870
ΔH_f (cal/g-atom) ^a	-475	-990	-1920	-2810	-3310	-3770
ΔS_f (e.u./g-atom) ^a	-0.35	-0.90	-2.0	-3.1	-3.7	-4.3
$\bar{H}_H - F^\circ_{H_2}/2$ (cal/g-atom) ^b	-3950	-3150	-2500	-2250	-2000	-1600
$\bar{H}_H - H^\circ_{H_2}/2$ (cal/g-atom) ^b	-10680	-11560	-11920	-13020	-13440	-14400
$S_H - S^\circ_{H_2}/2$ (e.u./g-atom) ^b	-10.0	-12.5	-14.0	-16.0	-17.0	-19.0

^a For 1 g-atom Nb-H solid solution.

^b For 1 g-atom of hydrogen.

TABLE IV
RESULTS OF X-RAY DIFFRACTION ANALYSIS ON DIFFERENT Nb-H ALLOY COMPOSITIONS

Composition, atomic ratio N_H/N°	Phases identified	Lattice parameter ($\text{\AA}$)	Intensity of pattern
0.033	Single-phase: α - b.c.c.	3.308 ± 0.002	strong
0.050	Two-phase: α - b.c.c.	3.306 ± 0.005	strong
	β - b.c.c.	not computed	very weak
0.058	Two-phase: α - b.c.c.	3.310 ± 0.005	strong
	β - b.c.c.	not computed	very weak
0.165	Two-phase: α - b.c.c.	3.310 ± 0.005	strong
	β - b.c.c.	3.423 ± 0.002	medium
0.30	Two-phase: α - b.c.c.	3.314 ± 0.005	strong
	β - b.c.c.	3.413 ± 0.005	medium
0.50	Two-phase: α - b.c.c.	3.310 ± 0.005	strong
	β' - distorted b.c.c.	$\sim 3.422 \pm 0.005$	strong
0.70	Two-phase: α - b.c.c.	3.305 ± 0.005	weak
	β' - distorted b.c.c.	$\sim 3.410 \pm 0.005$	strong
0.82	Single-phase: β' - distorted b.c.c.	$\sim 3.409 \pm 0.005$	strong

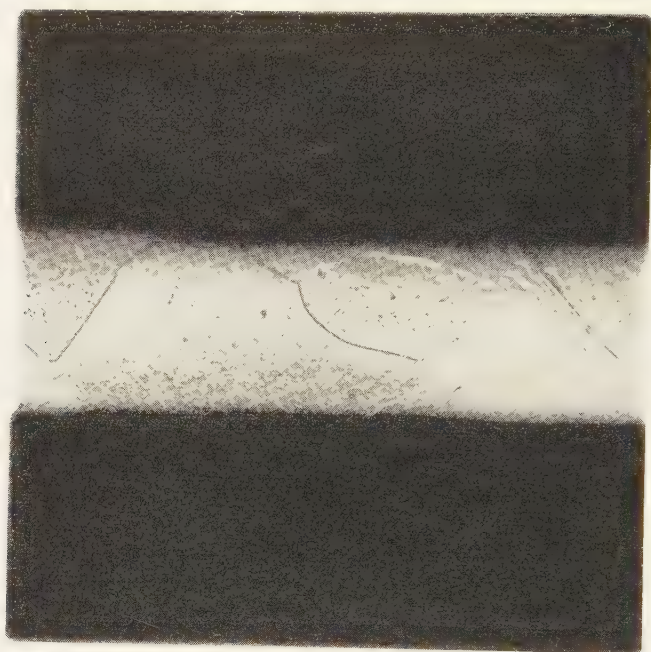


Fig. 6. Alloy Nb-0.033 atomic ratio H. Single-phase. $\times 1000$



Fig. 7. Alloy Nb 0.05 atomic ratio H. Matrix α -phase with small amount of β -phase. $\times 500$

Alloys with different hydrogen contents were produced by high-speed quenching. The alloys were equilibrated with hydrogen prior to the quenching in the temperature range 300°–900°C. X-ray diffraction analysis was performed on the quenched alloys at room temperature. Table IV summarizes the results of the X-ray diffraction analysis.

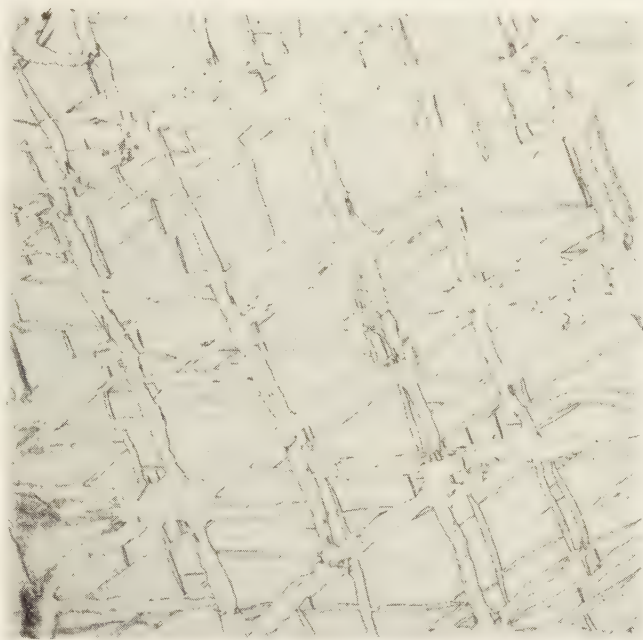


Fig. 8. Alloy Nb–0.30 atomic ratio H. α -phase with Widmanstätten-like β -phase. $\times 250$

The same alloys were examined metallographically. Typical microstructures are shown in Figs. 6–8. Alloy Nb–0.033 atomic ratio H, shown in Fig. 6, is single phase. Widmanstätten pattern second phase appears in increasing amount with increasing hydrogen content in alloys Nb–0.05 atomic ratio H (Fig. 7) and Nb–0.30 at. ratio H (Fig. 8).

DISCUSSION OF THE RESULTS

Since the composition of the niobium–hydrogen solid solution was found to be variant with the external hydrogen pressure within the entire range of the vapor-pressure measurements (Fig. 3), the system is a continuous solid solution in this temperature and concentration range. Similar conclusions were reported earlier^{6,7}, although the solubility data published are slightly lower than in this work. The higher solubility can be attributed to the higher purity niobium metal used in this investigation. Especially interstitial impurities were reported to reduce markedly the equilibrium hydrogen solubility of group Vb metals, as Ta and V^{17,18}.

Increasing equilibrium hydrogen pressure resulted in increasing hydrogen con-

centration of the single-phase Nb-H solid solution. Increasing temperature resulted in lower solubility.

The composition *vs.* square-root equilibrium hydrogen pressure relationship deviates from linearity in the temperature range 300°–600°C between compositions 0.1–0.8 atomic ratio $N_{\text{H}}/N_{\text{Nb}}$, as is indicated by the corresponding isotherms on Fig. 3. The deviation from linearity gradually increases with sinking temperature. The slope of the isotherm for 300°C between compositions 0.1–0.6 atomic ratio $N_{\text{H}}/N_{\text{Nb}}$ is the most gradual, as is shown in Fig. 4. This indicates that the temperature is not much above a possible invariancy of the system, resulting in a two-phase field on the equilibrium



Fig. 9. Alloy Nb-0.82 atomic ratio H. Martensite-like plate enclosed by polygonal matrix
Possibly $\beta + \beta'$. $\times 1000$

diagram. Similar isotherms were found in the Pd-H¹⁹ and Zr-H²⁰ systems just above the temperature where the transition from metal hydride to solid solution occurs. The deviations from linearity of the isotherms were treated by statistical mechanical methods for the Pd-H and Zr-H systems^{21,22} and have been attributed to attractive interactions between neighboring hydrogen atoms. In the case of increasing bond energy between atoms, clustering can be expected — especially at lower temperatures. Furthermore, if the solute atoms interact attractively, the greatest dependence of the heat of solution on composition would occur at the highest hydrogen concentrations.

The thermodynamic data presented in Table III for 400°C show that the partial

heat of solution increases with increasing hydrogen content of the solid solution. The increasing exothermic characteristics of the formation of the Nb-H solid solution is clearly illustrated in Fig. 5, with the increasing slopes of the isopleths toward the highest hydrogen concentrations.

It is unfortunate that the accuracy of the vapor-pressure measurements below 300°C was not adequate to compute reliable thermodynamic data for a wide composition range, where the study of the deviation from ideality would be the most desirable. This inaccuracy is the result of prolonged time requirements to reach equilibrium due to slow diffusion below 400°C.

It was mentioned in the previous sections that alloys with different hydrogen composition were produced by high-speed quenching after equilibrium was reached between 300° and 900°C. In view of the results of the SIEVERTS-type experiments all the alloys listed in Table IV were single-phase alloys at the equilibrium temperatures prior to quenching. In spite of the extremely rapid quenching, the single-phase structures could not be retained at room temperature between compositions 0.05 and 0.82 atomic ratio N_H/N_{Nb} . Both X-ray diffraction analysis and metallographic examination revealed two-phase structures. The high speed of the quenching process and the slow diffusion of hydrogen in niobium below 400°C temperature was formerly emphasized. Therefore it is evident from these experiments that the diffusion cannot be the controlling mechanism in the formation of the coexisting two b.c.c. phases — α and β — from the single-phase solid solution at low temperatures.

Furthermore, it is interesting to note the composition dependence of the appearance of the distorted b.c.c. phase in the quenched alloys. X-ray diffraction analysis indicated the existence of the β' phase between 0.5 and 0.82 atomic ratio N_H/N_{Nb} . Table IV lists all the alloys which contained the α phase and the β' phase as distorted b.c.c. structure with lattice parameters close to the lattice parameter of the b.c.c. β phase, indicating slight degree of distortion. Actually the splitting of the original b.c.c. diffraction lines was restricted to the back-reflection part of the X-ray pattern.

Diffraction readings at high sensitivity failed to indicate the existence of the β' phase in alloys Nb-0.058 atomic ratio H and Nb-0.30 atomic ratio H. This confirms the composition dependence of the β' phase, which phenomenon cannot be fitted within a normal miscibility gap. A stabilization effect of the hydrogen on the β' phase is suspected, which is characteristic of diffusionless transformations.

It is emphasized that the distortion of the β' phase from the b.c.c. β phase is very small. Even in the diffraction pattern of the alloy with the highest hydrogen composition (0.82 atomic ratio H), there were lines which could be indexed as b.c.c. structure and the rest of the lines were very close to it. The possibility exists that all alloys containing the β' phase contain β phase too. Metallographic examination of alloy Nb-0.82 atomic ratio H revealed coarse polygonal crystals enclosing elongated plates which resembled products of martensite transformation, as was formerly reported by PAXTON *et al.*¹¹.

In conclusion, the diffusionless characteristic of the formation of the $\alpha + \beta$ two-phase field below 300°C temperature, the possibility of clustering above this critical temperature, and the composition dependence of the appearance of the β' phase with the formerly reported experimental data^{7,11,13} supply evidence that the transformation is non-classical and does not obey the normal phase rule relationships. Martensitic and order-disorder transformations exhibit similar characteristics.

ACKNOWLEDGEMENT

Appreciation is expressed to the United States Atomic Energy Commission for sponsorship of this investigation under Contract Number AT(11-1)-515 and for permission to publish, and to Mr. DAVID WARWICK for his endeavors in the experimental investigation.

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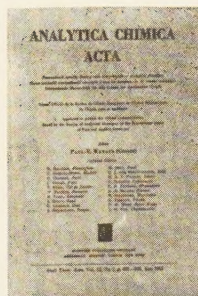
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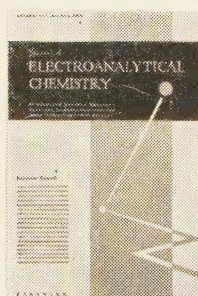


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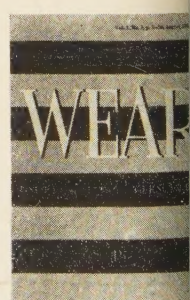
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